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THE UNIVERSITY OF ALBERTA

THE EFFECT OF THORIUM ON THE FERRIC-FERROUS COUPLE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

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UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read , and
recommended to the Faculty of Graduate Studies for acceptance
a thesis entitled

THE EFFECT OF THORIUM ON THE FERRIC-FERROUS COUPLE
submitted by J. H. BRECKENRIDGE in partial fulfilment of the
requirements for the degree of Doctor of Philosophy.

ABSTRACT

In the process of developing an analytical method for the amperometric titration of aluminum, using iron III as an amperometric indicator, it was found that thorium perchlorate interferes with the reduction of iron III at rotating palladium and platinum electrodes.

This interference was investigated using current voltage curves, radiochemical adsorption, chronopotentiometry and current pulse techniques. It is concluded that the primary effect of thorium is the reduction of the exchange current for the ferric-ferrous couple. It is postulated that the principal cause of this effect is the high charge carried by the thorium cation.

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LIST OF SYMBOLS

A	electrode area
$[Al^{+3}]$	moles of aluminum added to the solution as defined on page 14 (not molarity)
C	concentration
D	diffusion coefficient
F	Faraday
f	F/RT
i	current
i_A	current density
K	rate constant
n	Faradays per molar unit of reaction
R	gas constant
T	absolute temperature
$[Th^{+4}]$	moles of thorium added to the solution as defined on page 14 (not molarity)
t	elapsed time
α	transfer coefficient
η	overvoltage
ϕ_1	potential difference between the electrode and the inner Helmholtz layer
ϕ_2	potential difference between the electrode and the outer Helmholtz layer
τ	transition time

THE AMPEROMETRIC TITRATION OF ALUMINUM USING IRON III
AS AN AMPEROMETRIC INDICATOR

Few satisfactory methods exist for the amperometric determination of aluminum. Existing amperometric methods (25, 33, 37) are not applicable to small amounts or require an alcoholic medium for the titration. Because aluminum is not electroactive, an electroactive indicator or reagent will be required for its amperometric determination.

When neither the titrant nor titrate is electroactive, another substance which is electroactive can be added to the solution to indicate the end point. Such a substance is called an amperometric indicator. Thus Ringbom (33) added iron III to an alcoholic solution of aluminum which he then titrated with fluoride. Prior to the end point, Na_3AlF_6 precipitates. After the end point, the excess fluoride complexes with the iron III and consequently the iron III diffusion current decreases linearly with excess fluoride.

Aluminum interferes in many fluoride determinations by forming strong fluoride complexes. The fluoride method of Harris (23) is no exception. This titration uses iron III as an amperometric indicator and thorium as a titrant. The thorium fluoride complex is more stable than the corresponding iron III complex and the addition of thorium to a solution of iron III and fluoride liberates

iron III with an increase in the iron III reduction current until the end point is reached. Because aluminum fluoride complexes are about as stable as thorium fluoride complexes, aluminum, if present, makes the results for fluoride low. It seemed that it might be possible to use this interference of aluminum in the fluoride titration to determine traces of aluminum.

Initial attempts to reproduce the results of Harris were frustrated by a persistent background current which was about ten times larger than the change in current being measured. Careful purification of the reagents used in the titration did not eliminate the problem. Using redistilled water did not help either, but when the distilled water was treated with an ion exchanged resin to remove organic (non-ionic) materials, followed by a mixed cation-anion resin, the background current approached zero. This indicates that the background current was caused by an easily reducible non-ionic and distillable material, such as a chlorine compound used for water purification.

The effects of potassium sulfate, potassium bromide, and Aerosol OT on current voltage curves for iron III are shown in Figure 1. At the titration potential (+0.20 volts vs S.C.E.) both sulfate and bromide reduce the iron III diffusion current but Aerosol OT increases it. The principal effect of potassium bromide is to reduce the background current. Potassium sulfate improves the

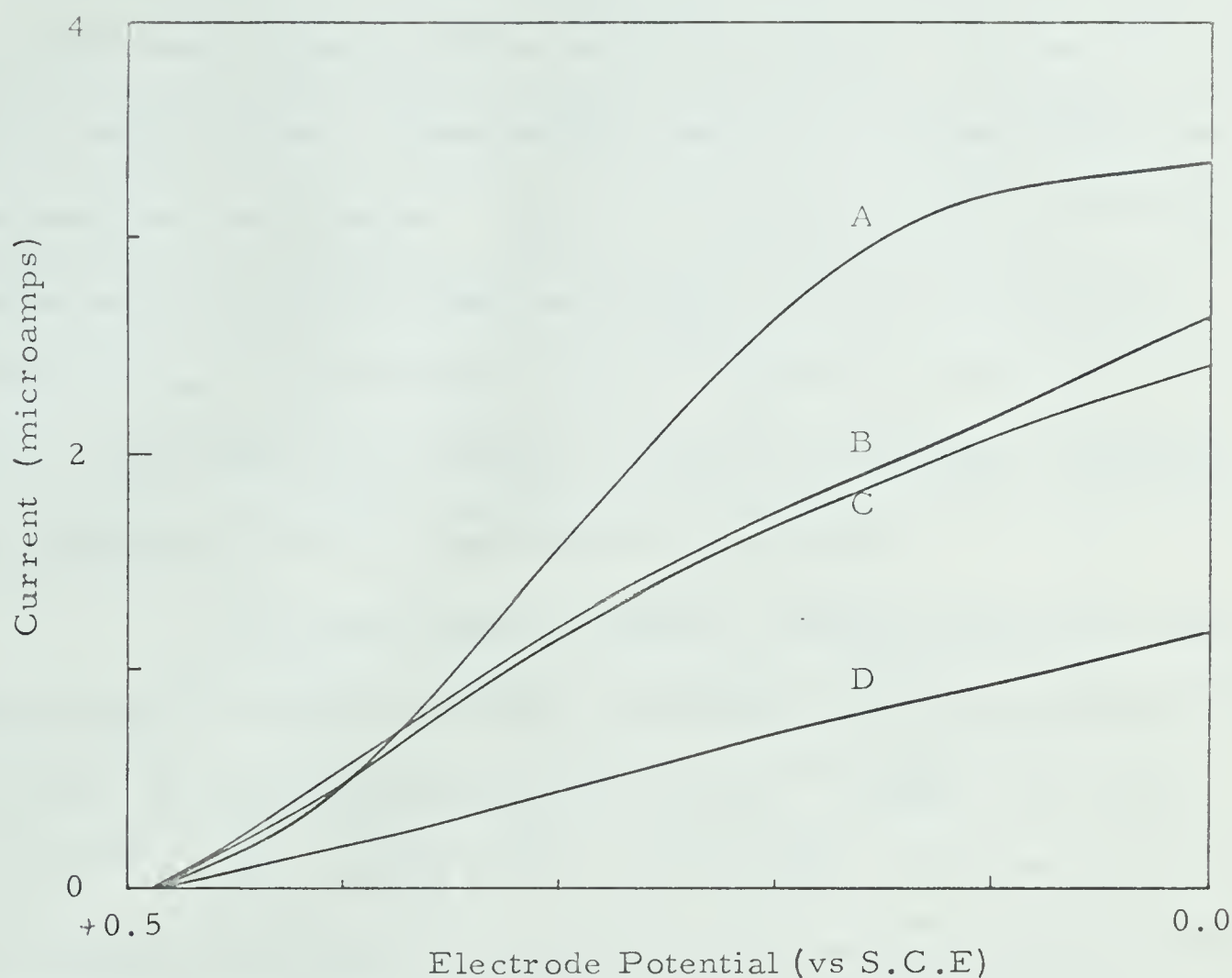


Figure 1. The effect of potassium bromide, potassium sulfate, and Aerosol OT on current voltage curves for ferric chloride at a rotating palladium electrode. pH 2.8 (monochloroacetic acid buffer).

A, 1.0×10^{-5} M, FeCl_3 ; 5×10^{-6} g/ml, Aerosol OT.

B, 1.0×10^{-5} M, FeCl_3 ; 5×10^{-6} g/ml, Aerosol OT; 8.0×10^{-3} g/ml, KBr.

C, 1.0×10^{-5} M, FeCl_3 ; 5×10^{-6} g/ml, Aerosol OT; 8.0×10^{-3} g/ml, KBr;
 5.0×10^{-4} g/ml, K_2SO_4 .

D, 1.0×10^{-5} M, FeCl_3 ;

(In this figure, as in subsequent figures containing current-voltage curves, small fluctuations in the curves were smoothed out during redrawing.)

(In general in this and subsequent figures the residual background current at the titration potential was about 0.2 to 0.3 μ amp. The rate of electrode rotation was usually about 1800 R.P.M..)

determination of the end point by reducing the tendency of the current to decline after the end point. The Aerosol 1B (sodium dibutyl sulfosuccinate) used originally (23) is no longer available. Aerosol OT (sodium dioctyl sulfosuccinate) is less soluble than Aerosol 1B especially when inorganic salts are present. Its lower solubility is offset by its higher surface activity so that a final concentration of 5×10^{-6} g/ml was as satisfactory as a concentration of 1×10^{-4} g/ml for Aerosol 1B. If higher Aerosol OT concentrations were used, the detergent coagulated when thorium perchlorate was added to the solution.

A combined solution of buffer, detergent potassium sulfate and potassium bromide was made up such that 5 ml of this solution contained 9.5×10^{-2} g monochloroacetic acid, 1.4×10^{-2} g NaOH, 0.40 g KBr, 5.0×10^{-2} g K_2SO_4 and 5.0×10^{-4} g Aerosol OT*. Five ml aliquots of this solution were added to solutions prior to their being diluted to 100 ml and titrated. Hereafter this solution is referred to as the buffer detergent solution. A stock ferric chloride solution 1.00×10^{-3} $FeCl_3$; 0.005M HCl was used to provide the iron III indicator.

The state of the electrode surface has a marked effect on the iron III current. If the electrode surface is clean the reduction of iron III is rapid and the rate of reduction at the electrode is diffusion limited at the titration-potential. As the electrode surface ages the rate of reduction of iron III becomes slower and the current voltage

*The reason for the effect of Aerosol OT is unknown. The use of such surface active materials in electroplating is well known but the reason for the effect of such materials is not well known. In this case one can only speculate that it is a surface effect.

curve becomes irreversible. Consequently the current at the end point is reduced. These effects are shown in Figure 2.

A careful study of the variables in the titration was undertaken to make it possible to choose conditions under which the fluoride to thorium ratio at the end point would be as reproducible as possible. This was necessary because the precision of a method for aluminum based on the fluoride titration would necessarily depend on the reproducibility of the fluoride titration. The effect of the variables on the aluminum interference was studied simultaneously with their effect on the fluoride to thorium ratio.

The influence of pH on the fluoride to thorium ratio at the end point is shown in Figure 3. It can be seen that as the pH increases so does the fluoride to thorium ratio. The recommended pH of 2.8 gives a fluoride to thorium ratio of 1.5 to 1. The pH effect shown in Figure 3* is probably caused by competition for fluoride ions by hydrogen ions. The ionization constant of hydrofluoric acid is larger than the ionization constant for thorium fluoride but hydrogen ions are present at a much higher concentration than thorium ions. Kolthoff, Meehan and Sambucetti (25) reported a similar effect in the amperometric titration of fluoride with aluminum using a rotating aluminum electrode. Thorium undergoes hydrolysis over the entire pH range covered in Figure 3. If thorium were increasingly hydrolyzed with increasing pH it would be less effective as a titrant for fluoride and the fluoride to thorium ratio would decrease

*It is not possible to predict the effect of pH on the fluoride to thorium ratio because the appropriate stability constants are not known with sufficient accuracy.

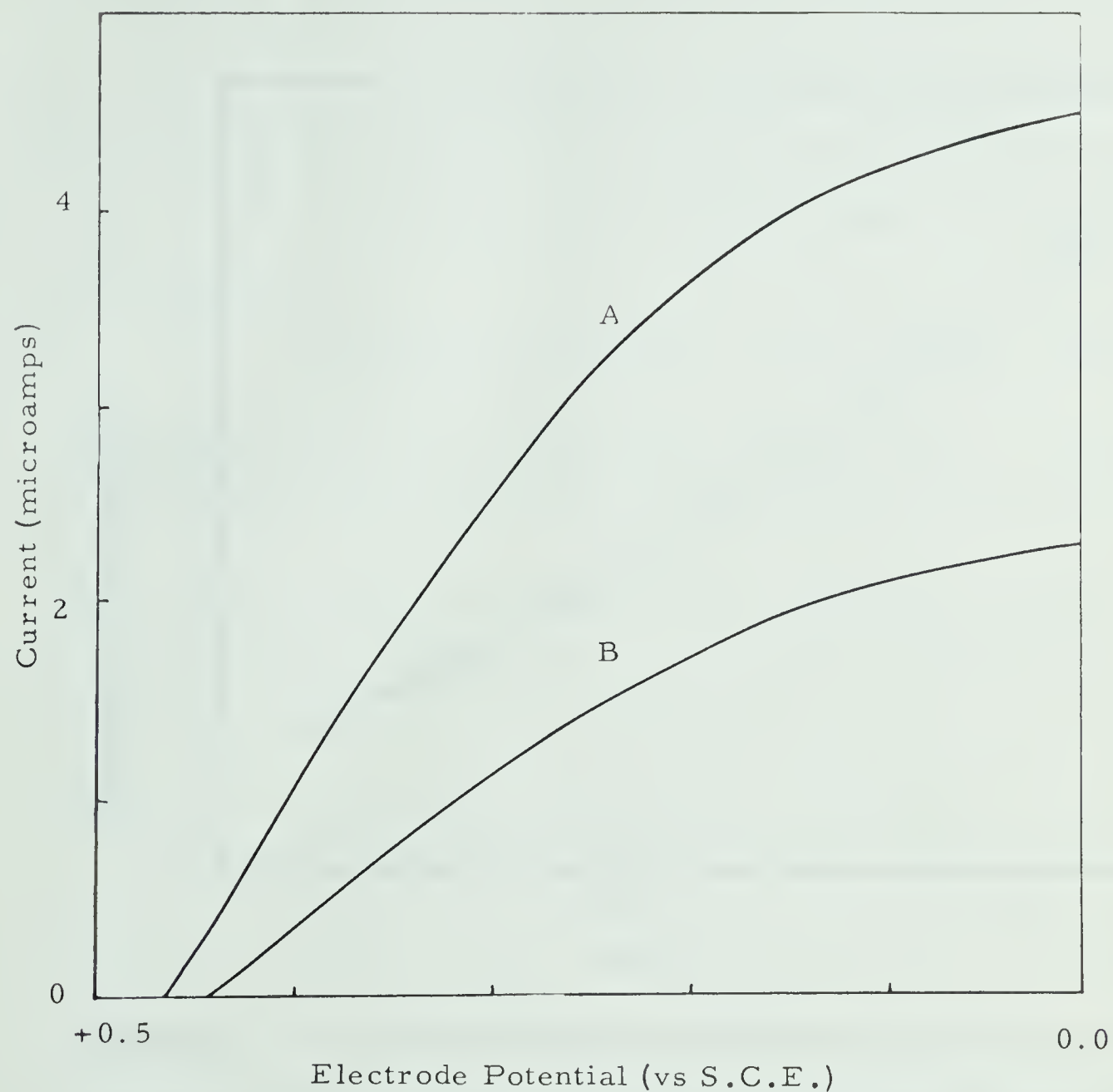


Figure 2. The effect of electrode surface on current voltage curves for iron III at a rotating palladium electrode. $1.0 \times 10^{-5} \text{M}$, FeCl_3 ; $4.0 \times 10^{-3} \text{ g/ml}$, KBr ; $5.0 \times 10^{-4} \text{ g/ml}$, K_2SO_4 ; $5 \times 10^{-6} \text{ g/ml}$, Aerosol OT; pH 2.8.

A, Freshly cleaned electrode.

B, Aged electrode.

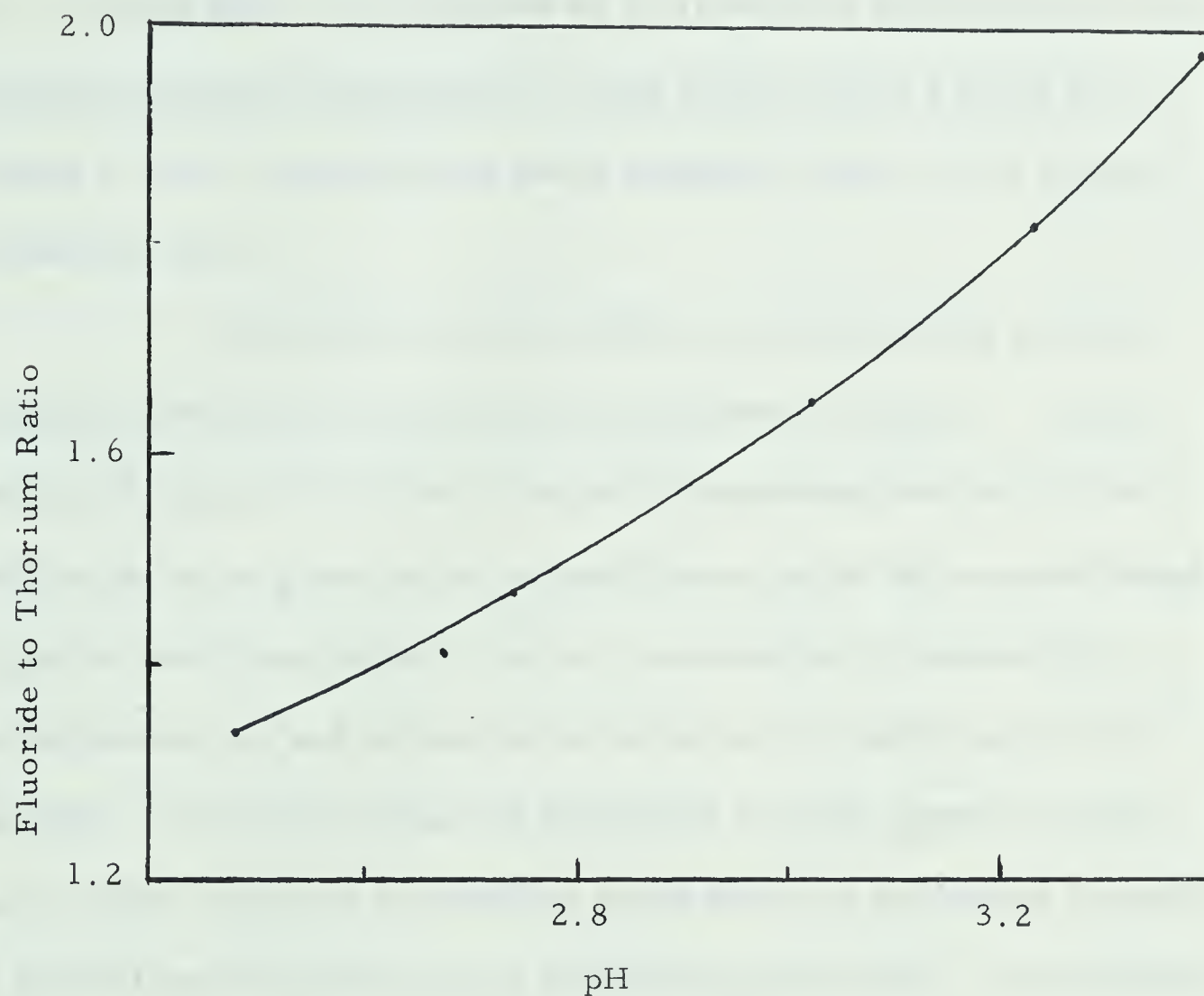


Figure 3. The effect of pH on the fluoride to thorium ratio at the end point in the amperometric titration of fluoride with thorium using a rotating palladium electrode. Each solution had a volume of 100 mls and contained 1.5×10^{-5} moles of NaF and 5 mls of buffer-detergent solution. The concentration of the ferric chloride indicator was 10^{-5} M.

with increasing pH. Figure 3 indicates the opposite trend and therefore hydrolysis of thorium is not an explanation for the variation in ratio with pH. The pH effect is not caused by a variation in buffer composition because in separate experiments it was shown that at a given pH a change in buffer concentration has a negligible effect on the fluoride to thorium ratio.

The effects of several other variables on the ratio of fluoride to thorium at the end point are shown in Table 1. In this table each value is the mean of several determinations (usually ten) and the deviation given is the standard deviation of the reported mean. It can be seen from Table 1 that the concentration of Aerosol OT, potassium sulfate and potassium bromide do not significantly affect the ratio. While the amount of potassium bromide present is not particularly important it should be noted that if no potassium bromide is present the end point ratio is substantially increased. No titration is possible without Aerosol OT because the iron III current is too low.

The electrode potential affects the apparent stoichiometry as shown in Table 2. During the titration a number of iron III complexes exist. Each of these complexes has a different reduction potential so that the contribution of these complexes to the measured reduction current is a complex function of electrode potential. As the potential of the electrode becomes more negative both iron III and iron III fluoride

TABLE 1. THE EFFECT OF SEVERAL VARIABLES ON THE
FLUORIDE TO THORIUM RATIO AT THE END POINT

FeCl_3 moles/liter	KBr grams/ml	K_2SO_4 grams/ml	Aerosol OT grams/ml	Fluoride to Thorium Ratio at the End Point*
1.00×10^{-5}	4.00×10^{-3}	5.00×10^{-4}	5.0×10^{-6}	1.597 ± 0.007
3.00×10^{-5}	4.00×10^{-3}	5.00×10^{-4}	5.0×10^{-6}	1.638 ± 0.013
1.00×10^{-5}	0	5.00×10^{-4}	5.0×10^{-6}	1.619 ± 0.020
1.00×10^{-5}	4.00×10^{-3}	5.00×10^{-4}	5.0×10^{-6}	1.513 ± 0.018
1.00×10^{-5}	4.00×10^{-3}	5.00×10^{-4}	5.0×10^{-6}	1.521 ± 0.011
1.00×10^{-5}	12.0×10^{-3}	5.00×10^{-4}	5.0×10^{-6}	1.536 ± 0.010
1.00×10^{-5}	4.00×10^{-3}	5.00×10^{-4}	5.0×10^{-6}	1.573 ± 0.04
1.00×10^{-5}	4.00×10^{-3}	15.0×10^{-4}	5.0×10^{-6}	1.520 ± 0.009
1.00×10^{-5}	4.00×10^{-3}	5.00×10^{-4}	5.0×10^{-6}	1.557 ± 0.011
1.00×10^{-5}	4.00×10^{-3}	5.00×10^{-4}	10×10^{-6}	1.568 ± 0.008

*All concentrations refer to the final titrated solution (volume 100 mls) which contained 1.50×10^{-5} mole of fluoride. All titrations were at pH 2.8.

TABLE 2. THE EFFECT OF ELECTRODE POTENTIAL ON THE
FLUORIDE TO THORIUM RATIO AT THE END POINT

<u>Electrode Potential (vs S.C.E.)</u>	<u>$[F^-] : [Th^{+4}]$ Ratio</u>
+ 0.30 volts	1.721 ± 0.007
+ 0.25 volts	1.574 ± 0.012
+ 0.20 volts	1.494 ± 0.005

complexes are reduced. Moreover, the end point of the titration does not coincide with any rigorous stoichiometric condition. Consequently the electrode potential influences the shape of the curve and the shape of the curve influences the apparent end point stoichiometry.

A study of the amperometric titration of aluminum based on its interference in the previously discussed fluoride titration was carried out. The results obtained for the aluminum interference depend on whether the aluminum is added to the fluoride solution before or after the iron III. If the aluminum is added to the fluoride solution after the iron III, the amount of fluoride consumed by the aluminum is much less than the amount consumed with the reverse order of addition. If the solution is allowed to stand for several hours the expected values for the aluminum interference are obtained. The results of the fluoride titration do not depend on the time elapsed between the addition of the iron III indicator and the titration with thorium. This must indicate that iron III fluoride complexes form relatively quickly and since the titration can be completed in less than a minute, these complexes must also dissociate quickly. Since iron III fluoride complexes react rapidly with thorium one would not expect these same fluoride complexes to react slowly with aluminum, as is apparently the case. One could speculate that if iron III is added to the solution prior to the aluminum there would be much less free fluoride immediately available for reaction

with the aluminum when it is added and consequently some of the aluminum may form hydrolysis complexes instead. These complexes are generally slow to react (20). Unfortunately such an argument can also be applied to the conditions that exist when thorium is added to a solution. However aluminum may hydrolyze more quickly or more extensively than thorium.

In the titration of fluoride with thorium the variable that is the most important and the most difficult to reproduce is the electrode surface. As the surface of the electrode becomes aged the fluoride to thorium ratio at the end point steadily increases and the iron III reduction current after the end point is increasingly subject to a post end point decrease in current caused by the excess titrant. Figure 4 shows three titration curves obtained with the same electrode and reagents. After each titration the electrode was aged by holding it in a concentrated ferric chloride solution at +0.20 volts (vs S.C.E.). The amount of current passed through the electrode and shown in Figure 4 is approximate because the current steadily decreased as the electrode aged.

During this aging process the shape of the titration curve changes in an undesirable manner (Figure 4). For example, in Figure 4C the end point cannot be precisely located because of the continually decreasing current after the end point.

Cleaning the electrode surface temporarily overcomes the

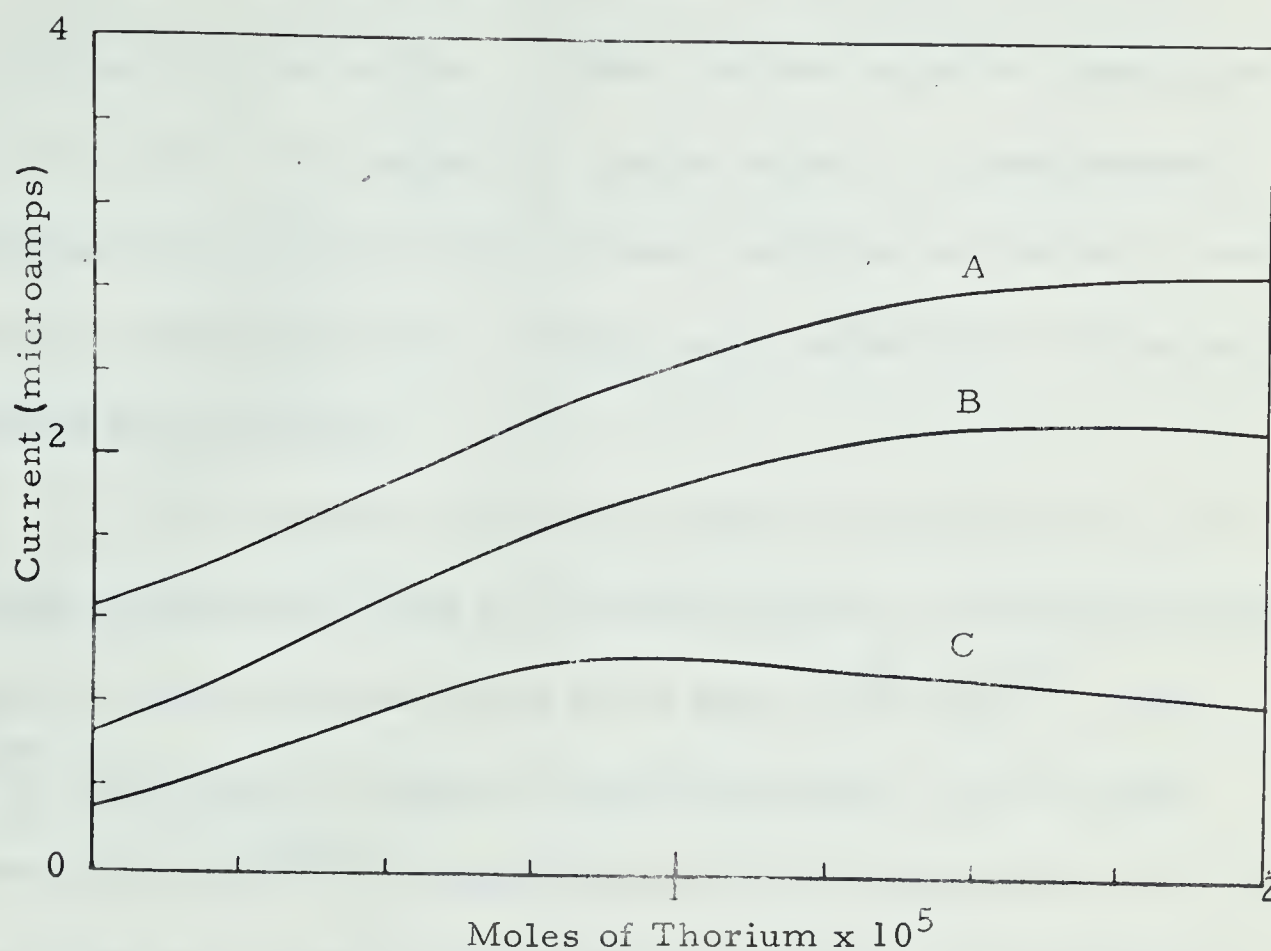


Figure 4. Titration curves for the titration of fluoride with thorium using a rotating palladium electrode of different ages and iron III as an amperometric indicator. Each solution contained 5 mls of buffer detergent solution and 1.5×10^{-5} moles of NaF in 100 mls of solution.

- A, Clean electrode, fluoride to thorium ratio at the end point 1.5.
- B, Electrode Age 0.2 amp-hr/cm^2 , fluoride to thorium ratio at the end point 1.7.
- C, Electrode Age 0.4 amp-hr/cm^2 , fluoride to thorium ratio at the end point 2.4.

effect of aging and reduces the depression effect. A vigorous cleaning (ten minutes in warm aqua regia) almost completely removes the depression effect for a time. Other effective forms of cleaning are hot nitric acid, warm potassium cyanide solution or polarization to potentials where the electrode surface is oxidized and oxygen is evolved. Chemical cleaning produces a longer lasting effect than electrochemical oxidation and reduction.

The feasibility of using the aluminum interference in the fluoride titration as a basis for the determination of aluminum depends primarily on the reproducibility of the ratio $\frac{[Al^{+3}]}{\Delta [Th^{+4}]}$ where $[Al^{+3}]$ represents the moles of aluminum present in the fluoride titration and $\Delta [Th^{+4}]$ is the difference in the thorium titer (in moles) when aluminum is present and when it is absent. The value of this ratio depends primarily on the relative amounts of fluoride in the aluminum and thorium complexes at the end point. Let us assume that A moles of fluoride are complexed with one mole of aluminum and that B moles of fluoride are complexed with one mole of thorium at the end point. Because the fluoride to thorium ratio obtained in the titration is essentially concentration independent, it can be concluded that the compositions of these complexes at the end point do not vary with concentration. If the reduction in the amount of fluoride available for titrating caused by the introduction of $[Al^{+3}]$ moles of aluminum is $\Delta [F^-]$ then

$$\Delta [\text{Th}^{+4}] = \frac{\Delta [\text{F}^{-}]}{B}$$

but $\Delta [\text{F}^{-}] = A [\text{Al}^{+3}]$

therefore $\Delta [\text{Th}^{+4}] = \frac{A [\text{Al}^{+3}]}{B}$

From which $\frac{[\text{Al}^{+3}]}{\Delta [\text{Th}^{+4}]} = \frac{B}{A}$

Only if the complexes had the same composition at the end point would $[\text{Al}^{+3}] / \Delta [\text{Th}^{+4}]$ be one. In any case the most important thing is that the ratio be reproducible; its absolute value is not of great concern.

Table 3 shows the effect of a number of variables on the ratio $[\text{Al}^{+3}] / \Delta [\text{Th}^{+4}]$. As the apparent end point of the titration shifts with electrode age the amounts of various complexes present at the end point will also change. Because the apparent end point does not coincide with any stoichiometric condition it is not possible to calculate how B/A should depend on the end point of the thorium titration of fluoride. However, provided that aluminum and thorium react only with fluoride then as a first approximation one would expect $[\text{Al}^{+3}] / \Delta [\text{Th}^{+4}]$ to show less variation than either A or B as defined above, since both A and B should have the same trend as the free fluoride concentration at the end point changes. Figures 6-9 show that this is correct.

Figure 5 shows that at a fixed fluoride concentration $\Delta [\text{Th}^{+4}]$ is a linear function of $[\text{Al}^{+3}]$. The slope of the straight lines in

TABLE 3. THE EFFECT OF SEVERAL VARIABLES ON THE

$$\text{RATIO } \frac{[\text{Al}^{+3}]}{\Delta [\text{Th}^{+4}]}$$

<u>FeCl₃</u> <u>moles/liter</u>	<u>KBr</u> <u>grams/ml</u>	<u>K₂SO₄</u> <u>grams/ml</u>	<u>Aerosol OT</u> <u>grams/ml</u>	<u>$\frac{[\text{Al}^{+3}]}{\Delta [\text{Th}^{+4}]}$</u> <u>Ratio</u>
1.00 x 10 ⁻⁵	4.00 x 10 ⁻³	5.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.947 ± 0.016
3.00 x 10 ⁻⁵	4.00 x 10 ⁻³	5.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.888 ± 0.017
1.00 x 10 ⁻⁵	0	5.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.877 ± 0.012
1.00 x 10 ⁻⁵	4.00 x 10 ⁻³	5.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.843 ± 0.008
1.00 x 10 ⁻⁵	4.00 x 10 ⁻³	5.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.858 ± 0.010
1.00 x 10 ⁻⁵	12.0 x 10 ⁻³	5.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.940 ± 0.020
1.00 x 10 ⁻⁵	4.00 x 10 ⁻³	5.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.893 ± 0.012
1.00 x 10 ⁻⁵	4.00 x 10 ⁻³	15.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.829 ± 0.012
1.00 x 10 ⁻⁵	4.00 x 10 ⁻³	5.00 x 10 ⁻⁴	5.0 x 10 ⁻⁶	0.908 ± 0.011
1.00 x 10 ⁻⁵	4.00 x 10 ⁻³	5.00 x 10 ⁻⁴	10 x 10 ⁻⁶	0.890 ± 0.010

All concentrations refer to the final titrated solution which contained 1.50 x 10⁻⁵ moles of sodium fluoride and 5.38 x 10⁻⁶ moles of aluminum nitrate in 100 mls of solution.

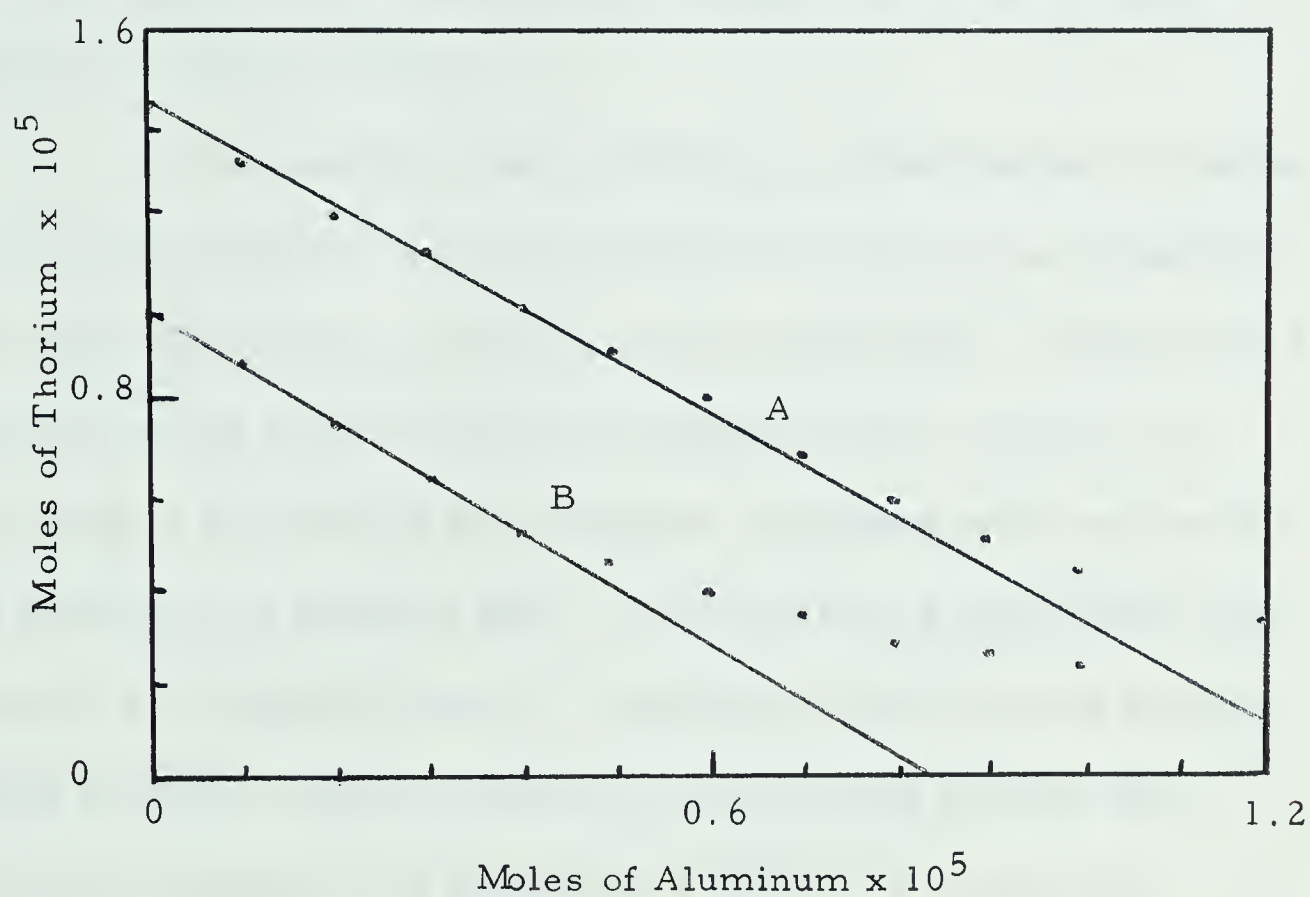


Figure 5. Moles of thorium required to reach the end point as a function of the moles of aluminum added to the solution at constant fluoride concentration. Each solution had a volume of 100 mls, contained 5 mls of buffer-detergent solution, and was 10^{-5} M in FeCl_3 .
A, 2.25×10^{-5} moles of sodium fluoride.
B, 1.5×10^{-5} moles of sodium fluoride.

Figure 5 is equal to $\Delta [\text{Th}^{+4}] / [\text{Al}^{+3}]$. This linear relationship holds until the aluminum concentration is about one third of the initial fluoride concentration. After this point $\Delta [\text{Th}^{+4}]$ declines. This linearity is desirable since it means that a linear calibration curve could be used for an analytical method.

If it is assumed that the variation of the fluoride to thorium ratio with pH is known, then it is possible to calculate the composition of the aluminum fluoride complex at various pH values. Figure 6 to 9 shows the results of four attempts to study the effect of pH on the composition of the thorium and aluminum complexes at the end point using electrodes of different ages. In these figures each point is the average of four determinations. The data for the aluminum fluoride complex are more scattered than the corresponding thorium data because the aluminum data depends on a difference between two titrations rather than on a single titration.

A typical relative standard deviation for a single measurement of the fluoride to thorium ratio is 2%. This means that the relative standard deviation of the $[\text{Al}^{+3}] / \Delta [\text{Th}^{+4}]$ ratio could not be less than about three percent. The average relative standard deviation for a single measurement of $[\text{Al}^{+3}] / \Delta [\text{Th}^{+4}]$ in Table 3 is 4%. This value is somewhat larger than expected; probably because the relative standard deviation of the fluoride titration increases with decreasing sample size. When aluminum is present the amount of fluoride

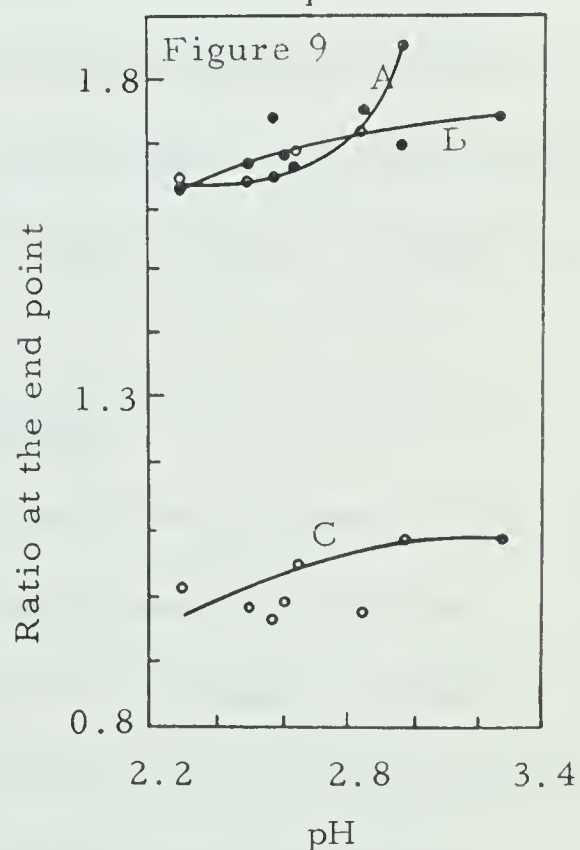
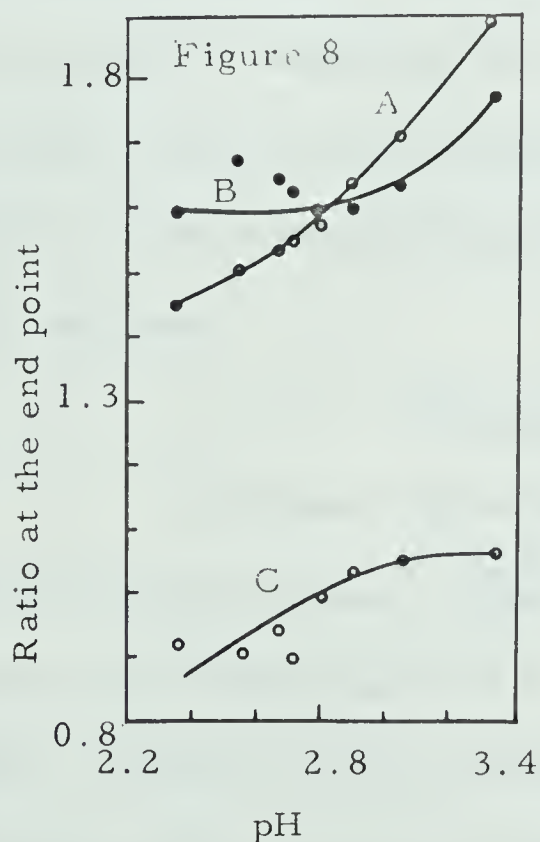
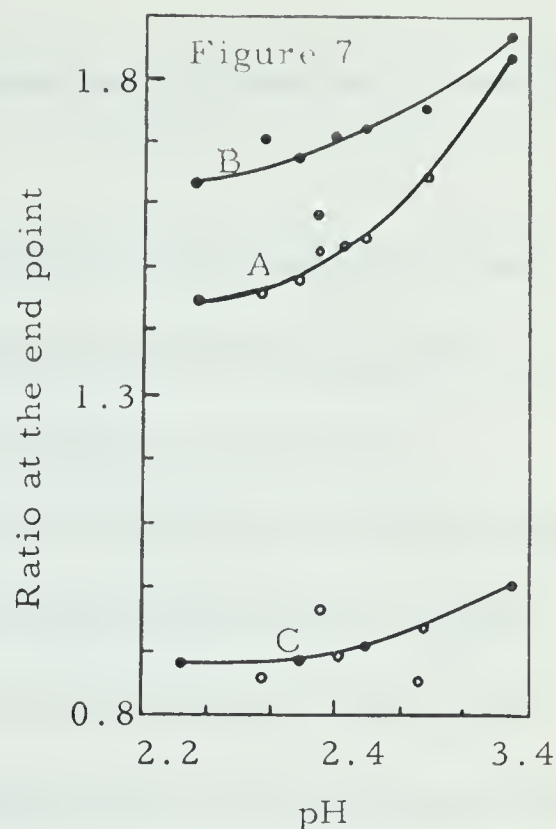
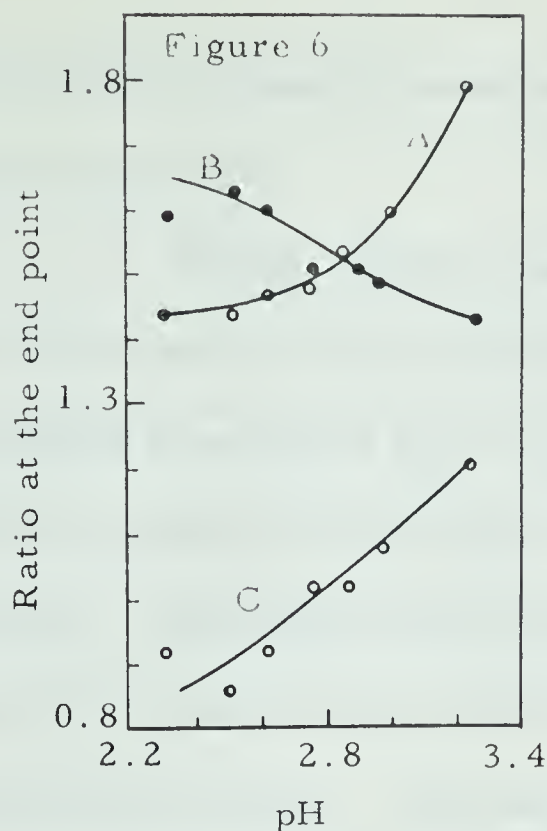


Figure 6-9. The effect of pH on the composition of the thorium and aluminum complexes and on the ratio $[Al^{+3}]/\Delta [Th^{+4}]$ for palladium electrodes of different ages. Each solution contained 5 mls of buffer-detergent solution and 1.5×10^{-5} moles of sodium fluoride in a volume of 100 mls. In addition to these reagents 5.4×10^{-6} moles of aluminum were present in every second solution titrated.

A, Fluoride to thorium ratio at the end point.

B, Fluoride to aluminum ratio at the end point.

C, $[Al^{+3}]/\Delta [Th^{+4}]$ ratio.

Figure 6, Clean electrode. Figure 7, Electrode age 0.01 amp hr/cm². Figure 8, Electrode age 0.1 amp. hr/cm². Figure 9, Electrode age 0.2 amp hr/cm².

available for titrating is lower because some of the fluoride is complexed with the aluminum.

Despite the fact that the apparent stoichiometry of the fluoride titration and the aluminum interference is not accurately predictable from day to day it should be possible to develop an analytical method for aluminum based on its interference in the fluoride titration. The method would involve the titration of a fixed amount of fluoride in the presence and absence of an aluminum standard and an aluminum unknown. The amount of aluminum in the unknown could be calculated by comparing the changes in thorium titer caused by an aluminum standard and the unknown. Such a method should be accurate to about 5% and it would possess the important advantage of simplicity and sensitivity.

Proposed Procedure

Into three 150 ml beakers pipet 15 mls of about 10^{-3} M sodium fluoride solution. Pipet an aliquot of unknown aluminum solution, containing about 100 micrograms of aluminum, into one beaker. Pipet an aliquot of standard aluminum solution (about 10^{-3} M) containing about as much aluminum as the unknown into a second beaker. Finally pipet 5 mls of buffer-detergent solution into all three beakers. Dilute each solution to a final volume of about 100 mls. Titrate each solution amperometrically with about 10^{-3} M thorium perchlorate solution using a rotating palladium electrode and a potential

of +0.2 volts (vs S. C. E.).

To calculate the weight (g) of aluminum in the unknown use the expression

$$\frac{\text{Titn. vol. F} - \text{Titn. vol. unknown}}{\text{Titn. vol. F} - \text{Titn. vol. std. Al}} \times \text{aliquot std. Al} \times M(\text{std.}) \times 0.027$$

Where titn. vol. F stands for the volume of thorium perchlorate solution required to reach the end point in the titration of the solution containing fluoride but no aluminum, and similarly for the other parts of the expression.

If the unknown is so dilute that an unduly large volume of unknown solution would be required it is recommended that a smaller volume of solution be used and that a proportionately smaller volume of fluoride also be used. The amount of aluminum in the solution titrated should not be less than about 20 micrograms nor more than 200 micrograms.

EXPERIMENTAL

With the exception of the Aerosol OT (which was supplied by American Cyanamid Company) and the perchloric acid (Baker and Adamson), Fisher certified reagent grade chemicals were used. Fluoride solutions were standardized with triphenyl tin chloride (38). Iron solutions were standardized gravimetrically. Disodium salt EDTA solutions were standardized with magnesium iodate (28).

Distilled water was treated with a Bantam Barnstead

Demineralizer using first the organic removal cartridge followed by a mixed resin cartridge. The final conductivity of the water was about $2 \times 10^7 \text{ ohm}^{-1}$. The cartridges were used in this order because the conductivity of the water leaving the organic removal cartridge was too high (10^5 ohm^{-1}).

Fisher certified reagent grade thorium nitrate was purified by precipitating thorium oxalate and redissolving it in hot perchloric acid. This purification was carried out at least twice. The reaction between perchloric acid and thorium oxalate is best controlled by slow heating and stirring to minimize foaming. Bumping is best prevented by stirring and by using a moderate excess of perchloric acid so that the slurry remains fluid. Small quantities were used for safety. Thorium solutions were standardized both gravimetrically and volumetrically (35). The amount of perchloric acid in the thorium perchlorate solutions was determined by converting thorium perchlorate to perchloric acid by way of a cation exchange resin and titrating the acid produced with sodium hydroxide. Since the thorium concentration was measured independently, the acid produced from the thorium could be calculated and the acid in excess of this amount was assumed to have been in the original solution.

Amperometric titrations were performed in an open 150 ml beaker. The reference electrode was a saturated calomel electrode with a rubber base (Figure 10). A Metrohm Polarecord model E261

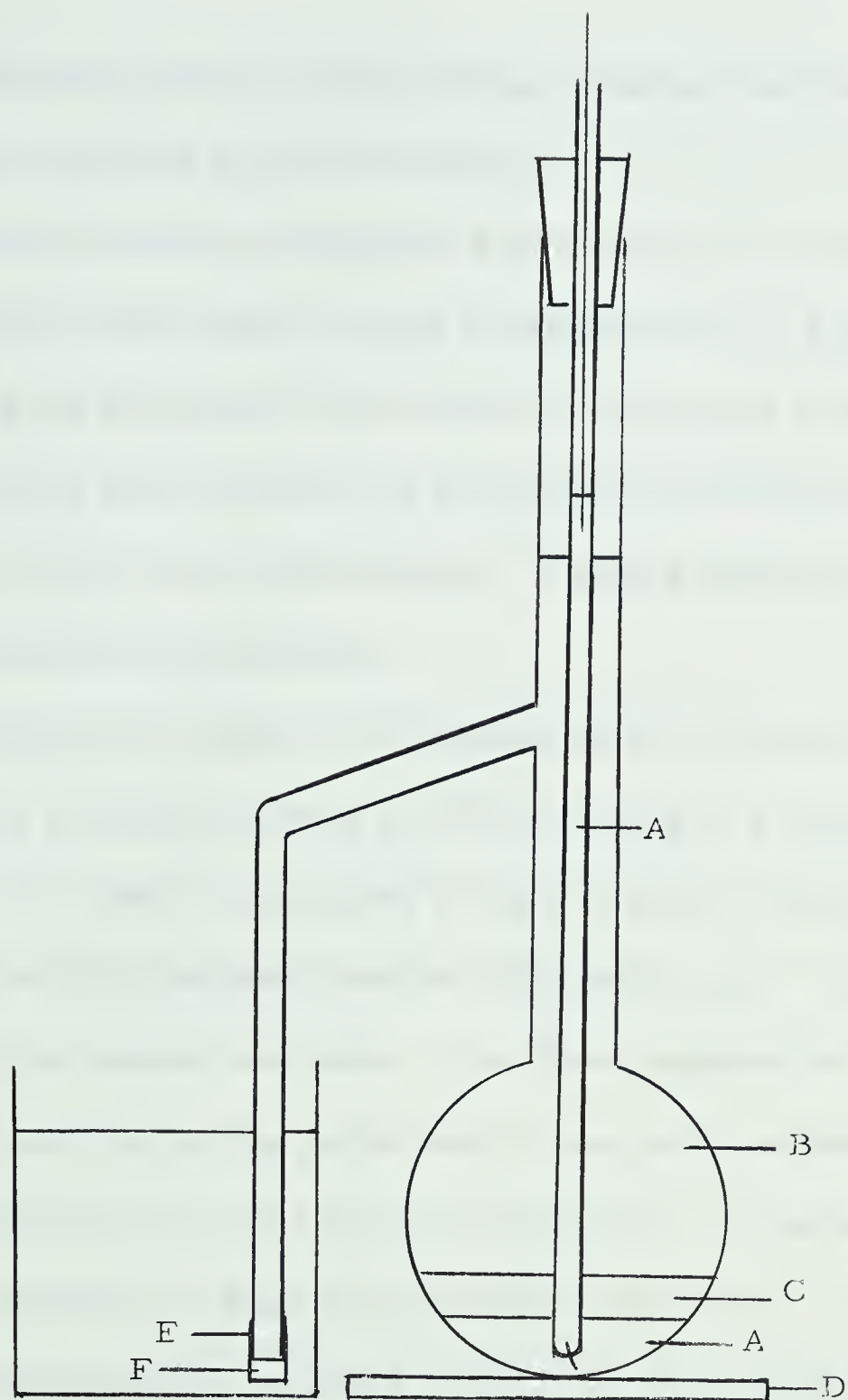


Figure 10. The S.C.E. reference electrode for amperometric titrations. A, mercury; B, saturated KCl solution; C, Hg_2Cl_2 , KCl; D, rubber base; E, rubber sleeve; F, porous glass

was used to control the potential of the rotating palladium electrode and to record the current as a function of time.

Because palladium amalgamates with mercury the rotating palladium electrodes were made by fusing a platinum wire to a palladium wire, then sealing the metal joint into the end of a soft glass tube so that the platinum wire made contact with the mercury inside the tube while the palladium wire was in the solution. Rotating palladium electrodes were used for all titrations.

The titrant was added to the solution from a constant flow buret. This buret proved convenient for the recording of a complete titration curve. End point rounding and the post end point decline in current could be carefully studied from the recorded curves. Two types of constant flow burets were used. The first consisted of a reservoir placed near the ceiling, to provide a large and constant head, connected to a capillary flow restrictor by tygon tubing. This arrangement was later replaced by a Sage Syringe Pump model 234-3. Buret flow rates were determined by an EDTA titration of the thorium delivered from the buret in a measured time. A concentrated thorium solution was used so that the maximum dilution error was less than 1%. This dilution error was so small that it could be ignored. The flow rate was such that a titration took about five minutes; shorter titration times produced excessively noisy titration curves.

When starting a series of titrations with a clean electrode,

the fluoride to thorium ratio at the end point increased steadily as the electrode aged. This increase was rapid at first and then became slower as the electrode aged. This effect combined with the dependence of the fluoride to thorium ratio on the surface meant that the ratio could not be exactly reproduced from day to day. It was therefore necessary to use the technique of alternation in studying the effect of a variable i.e. a standard solution was titrated alternately with a test solution. Hence the data in Tables 1 and 3 are grouped in pairs. Because alternation was used small differences between the values of a pair of data are significant. The standard deviations reported in Tables 1 and 3 are larger than would be expected in the absence of the systematic error resulting from the drift in stoichiometry.

AN INVESTIGATION OF THE CAUSES OF THE DEPRESSION OF THE
IRON III REDUCTION CURRENT AT THE ROTATING PALLADIUM
ELECTRODE

In the previous section dealing with the amperometric titration of aluminum, it was noted that the titrant (thorium perchlorate in perchloric acid) reduced the iron III diffusion current after the end point. One would hardly expect a cation such as thorium to influence the reduction, at positive potentials, of another cation such as iron III. Such an interference might be conceived at potentials more negative than the potential of null charge of a platinum electrode. This potential is about -0.14 to -0.04 volts (vs S.C.E.). At this potential, the charge on the electrode is zero and ideally, at more positive potentials anion adsorption occurs, while at more negative potentials cations are preferentially adsorbed. However the interference of thorium with the reduction of iron III occurs at +0.2 volts (vs S.C.E.) (the titration potential) and at potentials as positive as 0.5 volts (vs S.C.E.) (E^0 for the ferric-ferrous couple).

The possible causes of the depression effect which were investigated are:

1. The perchloric acid in the titrant.
2. Some impurity in the titrant which complexes with iron or blocks its reduction at the electrode.

3. The thorium perchlorate itself.

The possibility that the perchloric acid causes the depression effect was easily checked by adding some perchloric acid to an iron III solution and noting its effect on the current voltage curve for iron III. Figure 11 shows that the effect of perchloric acid is negligible if allowance is made for hydrogen reduction in 1M HClO_4 and hydrolysis in 0.001M HClO_4 . Using redistilled 60% perchloric acid to dissolve the thorium oxalate did not help. Adding perchloric acid, that had been heated to fuming, to an iron III solution did not produce the effect either, so a decomposition product of perchloric acid is not responsible for the effect.

An impurity in the titrant seemed to be a logical explanation of the depression effect and a considerable effort was made to purify the thorium perchlorate used in the titration, to no avail, as described below.

Oxalate could be a potential impurity. To eliminate this possibility the sides of the beaker used to dissolve the thorium oxalate were washed repeatedly and the solution was reheated to fuming after each washing, to destroy residual traces of oxalate. This did not reduce the depression effect. In an attempt to remove both cationic and anionic impurities, such as phosphate, thorium oxalate was precipitated by adding thorium to oxalate, then oxalate to thorium for a total of up to six precipitations. The addition of thorium to an oxalate

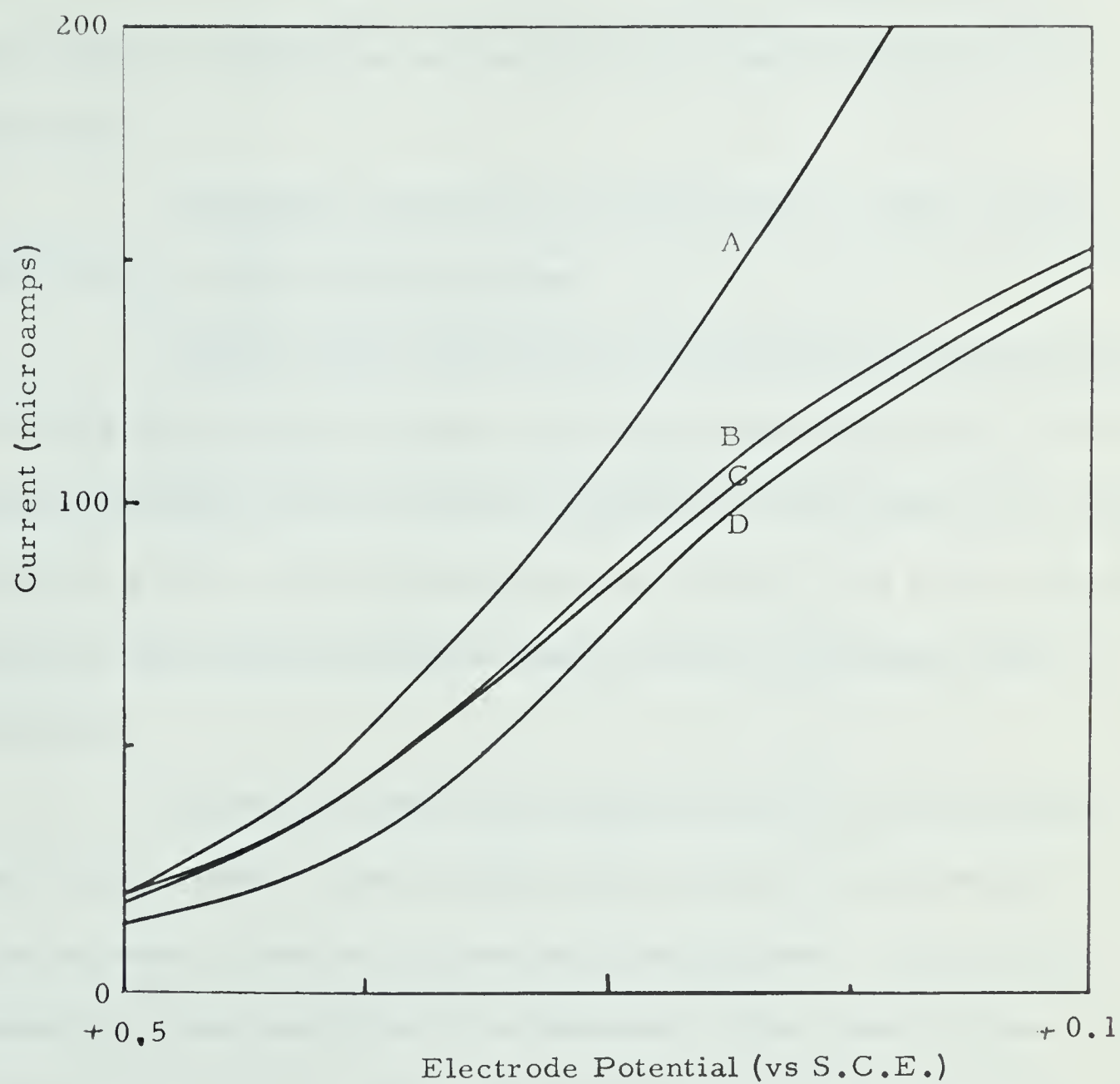


Figure 11. The effect of perchloric acid concentration on current voltage curves for iron III at a rotating palladium electrode. $1.9 \times 10^{-3}\text{M}$, FeCl_3 ; 0.1M , NaClO_4 ; HClO_4 ; A, 1.0M ; B, 0.10M ; C, 0.01M ; D, 0.001M .

solution should eliminate most anionic impurities from the precipitate. The reverse order of addition should eliminate cationic impurities. The depression effect was not reduced by this extensive purification procedure.

Treatment of thorium perchlorate with an anion exchange resin did not reduce the effect either.

Another batch of thorium was precipitated in five fractions. If a trace impurity were present that strongly adsorbed on the thorium oxalate precipitate then the impurity should be concentrated in the first fractions and the last fractions should be relatively free of the impurity. However each fraction produced nearly the same depression effect (Table 4).

Attempts to detect and measure likely specific impurities were not successful. For example large amounts of thorium perchlorate were titrated with potassium permanganate. No permanganate was consumed although the depression effect was such that had it been caused by oxalate, a few milliliters of permanganate would have been consumed by the samples taken.

Thorium solutions were amperometrically titrated with iron III. Had an impurity such as phosphate been present and had it been reacting with iron III a reversed L titration curve such as

TABLE 4. THE EFFECT OF CONSECUTIVE THORIUM PERCHLORATE
FRACTIONS ON THE REDUCTION OF IRON III

<u>Fraction</u>	<u>% Change in Diffusion Current</u>
1	65%
2	67%
3	65%
4	61%
5	63%

The change in diffusion current at a rotating palladium electrode was measured at +0.3 volts (vs S.C.E.) and at a pH of 2.8 (mono-chloroacetic acid buffer). $\text{Fe}(\text{Cl})_3$, 10^{-5}M ; Aerosol OT, 5×10^{-6} g/ml.

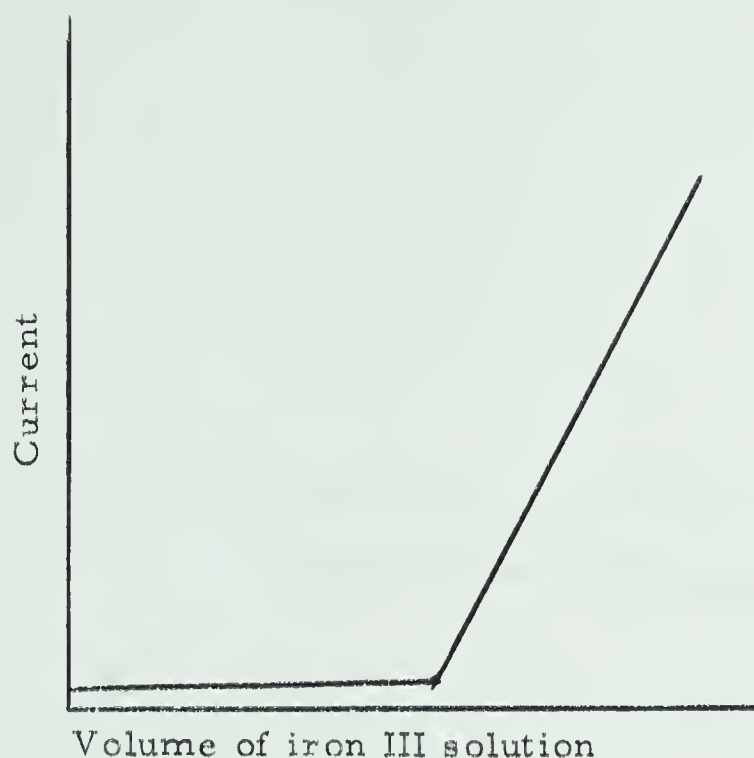


Figure 12.

Figure 12 should have resulted. The results were complicated by the fact that the electrode was insensitive to iron III and the sensitivity declined with time when thorium was present. No curves of the type shown above were obtained but in the light of the conclusions presented later in this thesis it is by no means certain that an impurity could be titrated with iron III in the presence of such a large excess of thorium

During attempts to either detect or eliminate an impurity some facts came to light which indicated that the iron III reduction current depression was not due to an impurity but was caused by thorium itself. In a fluoride titration the extent of the current depression is a linear function of the amount of thorium added in excess. For example in Figure 13 the iron diffusion current decreases linearly in the region from 2×10^{-5} moles of thorium to 4×10^{-5} moles of thorium. This would be expected if a trace impurity (for example

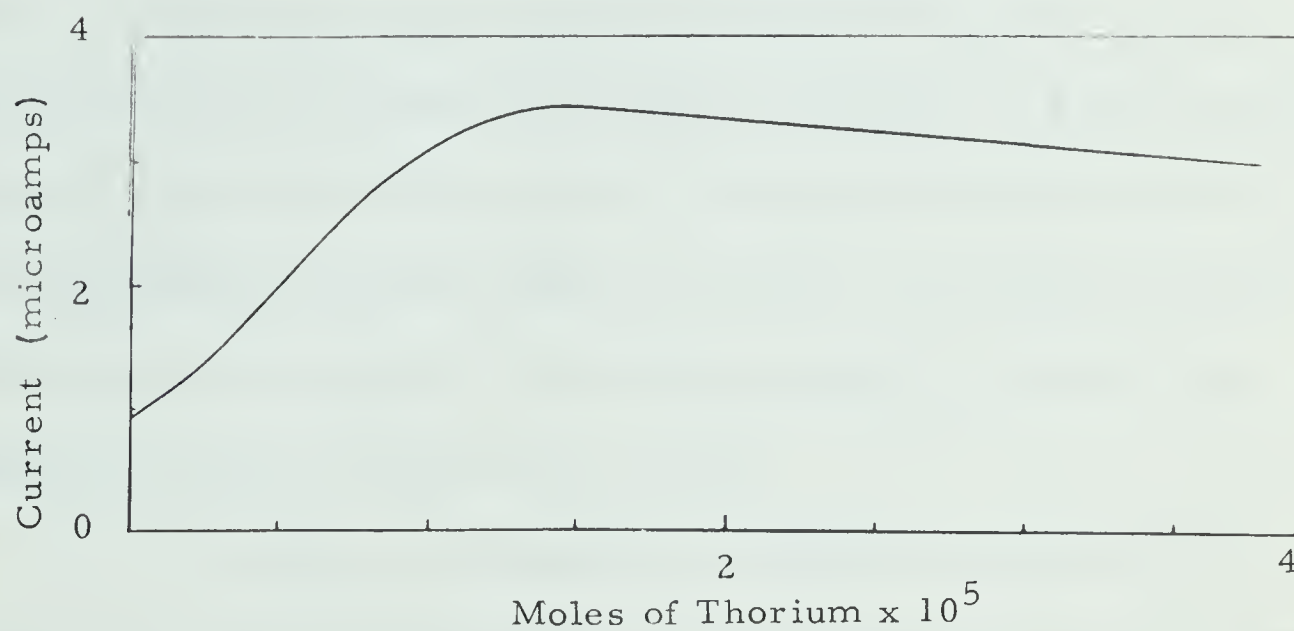


Figure 13. A titration curve, for 1.5×10^{-5} moles of NaF in 100 mls of solution containing 5 mls of buffer detergent solution, showing the linearity of the depression effect at a rotating palladium electrode. $1.0 \times 10^{-5}M$ $FeCl_3$.

phosphate) were present in the titrant. If thorium is added to a fluoride free solution of iron III the effect is no longer linear but is exponential (Figure 14). This could not result from the formation of a stoichiometric complex although it would result from the formation of a series of complexes such as $\text{Fe}(\text{X})_n$ where n ranges from about 1 to 5. Moreover the percentage change induced in the iron III reduction current by a fixed concentration of thorium, at a given potential, is fairly independent of the amount of iron present even though the iron III concentration is greater than the thorium concentration (Table 5). This would not be expected if the depression effect were due to an impurity forming a complex with iron III.

The idea of a complexing impurity is also inconsistent with the fact that the initial purity of the thorium nitrate was at least 99.8%. On this basis the impurity concentration could not exceed 0.2% of the thorium concentration and this amount is too little to produce the observed depression effect by complex formation.

The depression effect depends on the nature of the electrode surface. At a freshly cleaned electrode the effect of thorium on a current voltage curve for iron III is small. At an aged electrode where the reduction of iron III is highly irreversible, the effect of thorium is drastic. For example in Figure 15 a thorium concentration of $1.00 \times 10^{-3} \text{ M}$ decreased the iron III reduction current by 9% at 0.3 volts at a clean electrode; with an aged electrode the corresponding

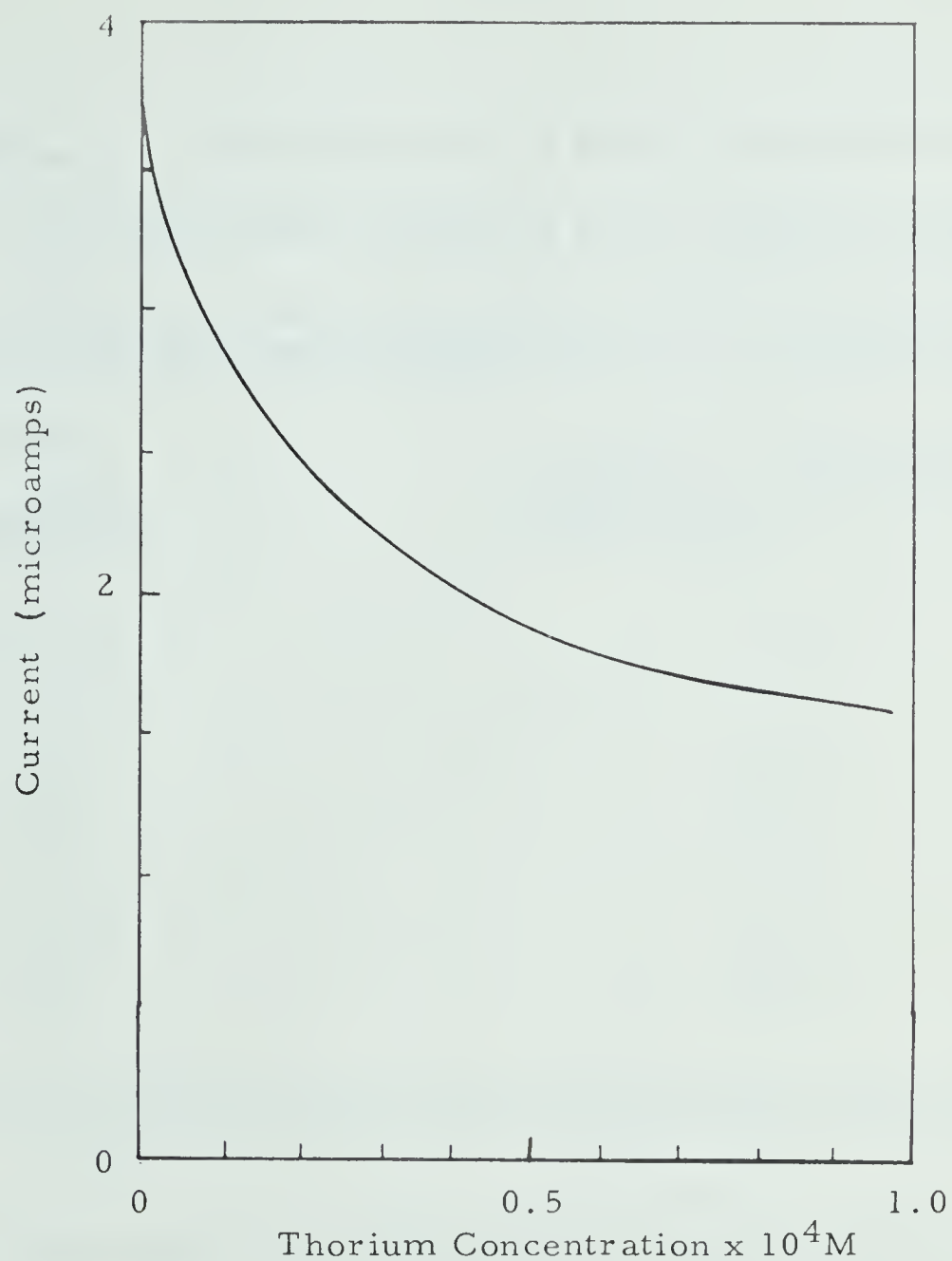


Figure 14. The effect of thorium perchlorate on the reduction current of iron III, at a rotating palladium electrode in a fluoride free system. The solution was 10^{-5} M in FeCl_3 and contained 5 mls of buffer detergent solution in a volume of 100 mls.

TABLE 5. THE EFFECT OF A FIXED AMOUNT OF THORIUM
ON THE REDUCTION CURRENT FOR VARIOUS AMOUNTS OF
IRON III AT A ROTATING PALLADIUM ELECTRODE

<u>Fe(ClO₄)₃</u> <u>(moles/liter)</u>	<u>% Change in Reduction Current</u> <u>Induced by 1.00 x 10⁻⁴M Thorium</u> <u>Concentration</u>
9.5 x 10 ⁻⁵	18%
1.9 x 10 ⁻⁴	37%
9.5 x 10 ⁻⁴	35%
1.9 x 10 ⁻³	24%
3.8 x 10 ⁻³	28%

The solution was 0.05M HClO₄ and the change in current was measured at +0.30 volts (vs S.C.E.).

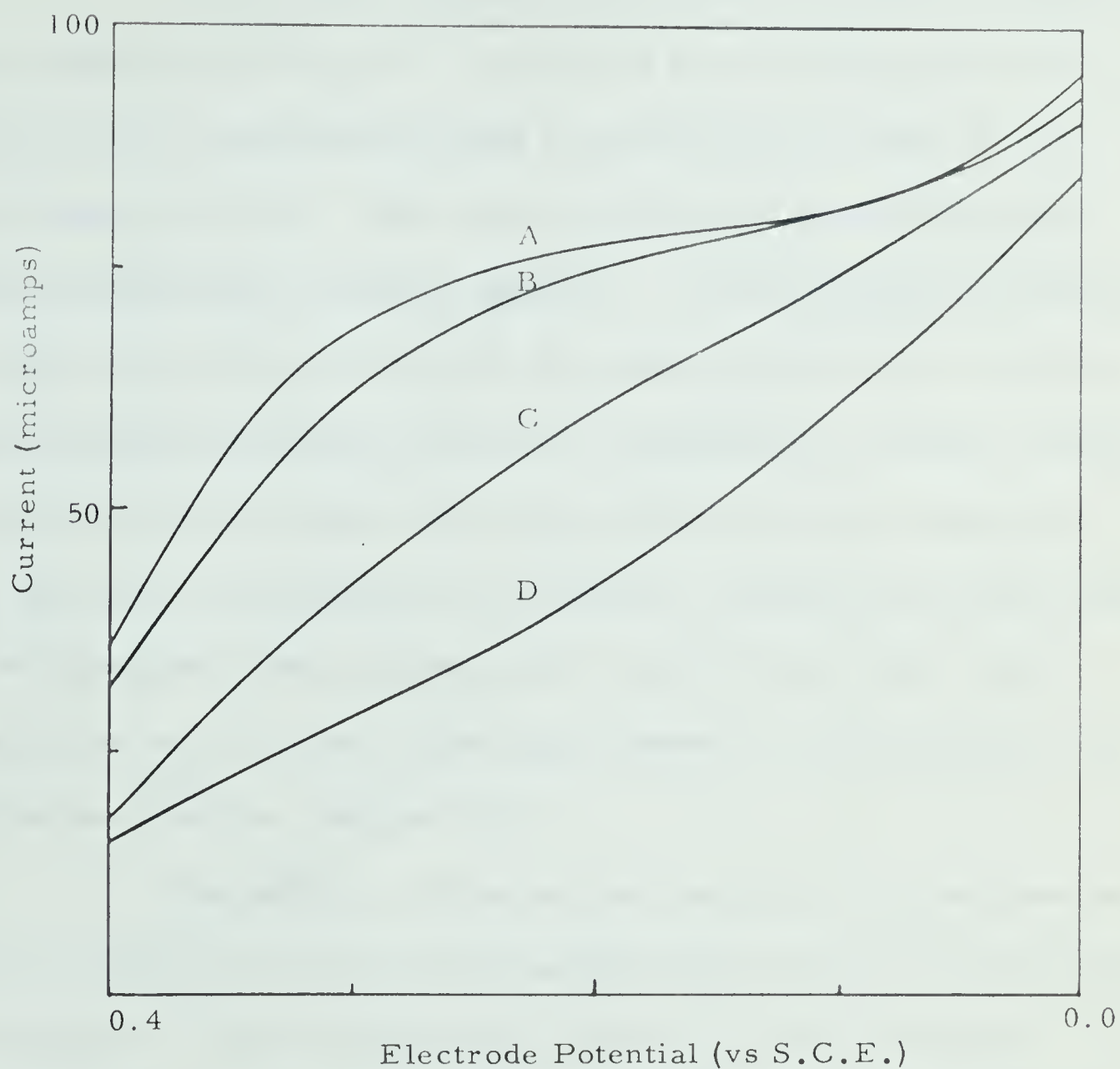


Figure 15. The effect of thorium on the reduction of iron III at a clean and aged palladium electrode. All solutions were $1.0 \times 10^{-4}\text{M}$, $\text{Fe}(\text{ClO}_4)_3$; 0.05M , HClO_4 . In addition the solutions used for current voltage curves B and D were $1.0 \times 10^{-4}\text{M}$, $\text{Th}(\text{ClO}_4)_4$.

A, B, Clean electrode.

C, D, Aged electrode.

decrease is 30%.

At this point a platinum electrode was tried as a replacement for a palladium electrode. The effect of thorium on the reduction of iron III at a platinum electrode is qualitatively the same as at a palladium electrode. This is not surprising because both platinum and palladium have similar properties. It is not possible to quantitatively compare the effect of thorium on the reduction of iron III at platinum and palladium electrodes because it is not possible to prepare platinum and palladium electrodes with surfaces that are exactly comparable. In any case in the original work on fluoride, palladium was used because "the undesirable effects appear to be least with electrodes made of palladium and to become increasingly greater with 90% platinum-10% rhodium, platinum, and gold" (23).

The addition of fluoride to an iron III solution reduces the iron III diffusion current by forming difficult-to-reduce iron III fluoride complexes. However if fluoride is added to an iron III-thorium solution the iron III current is actually increased up to a point (Figure 16). Since thorium fluoride complexes are more stable than iron III fluoride complexes (4) it appears that thorium complexed by the fluoride is no longer available to interfere with the reduction of iron III. Consequently the iron current increases. It would be difficult to explain the effect of fluoride in any other way.

The previous experimental evidence rules out the possibility

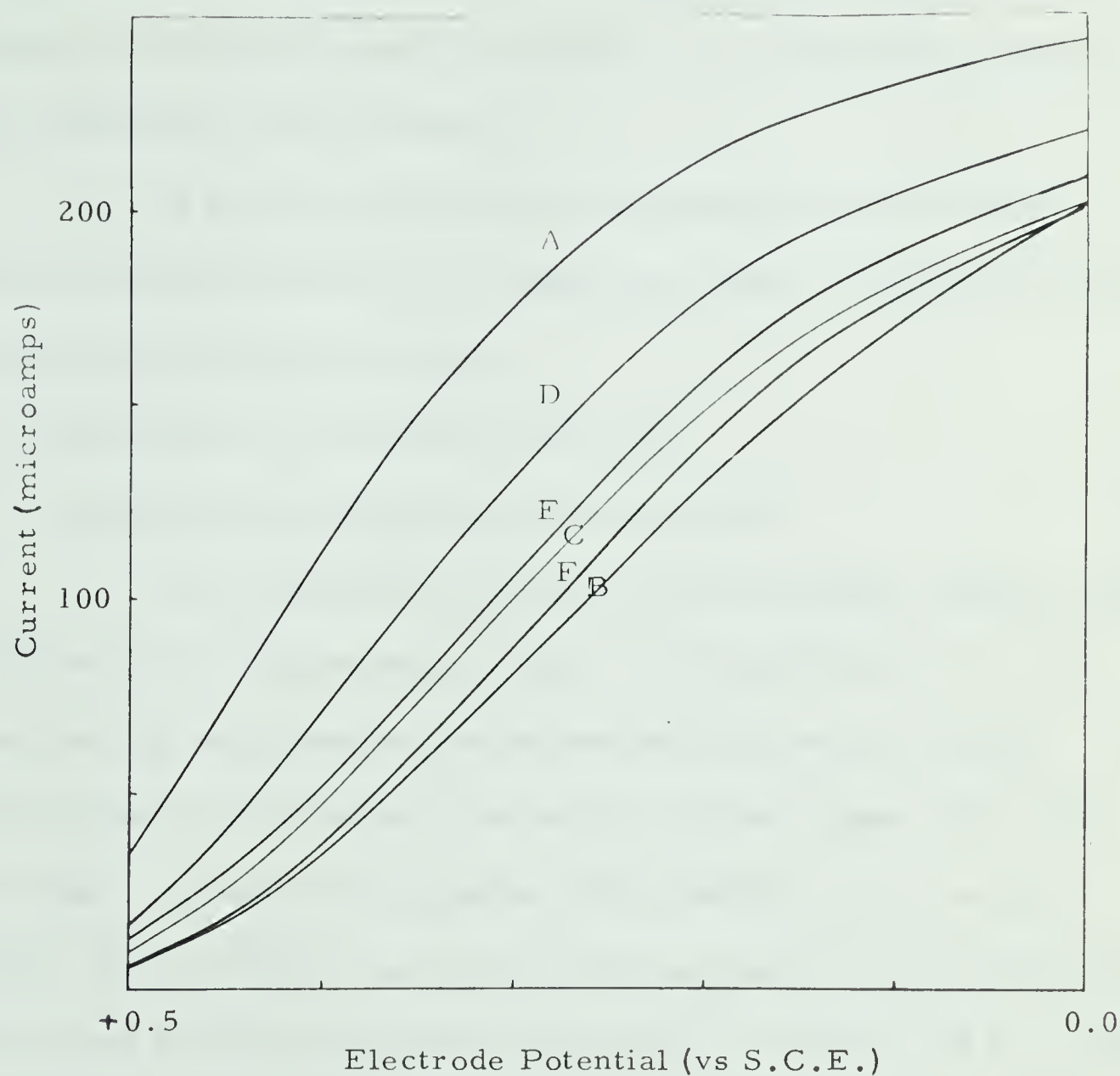


Figure 16. The effect of fluoride on current voltage curves for iron III in the presence of thorium at a rotating platinum electrode. Solutions were 0.05M, HClO_4 and $2.47 \times 10^{-3}\text{M}$, $\text{Fe}(\text{ClO}_4)_3$. A, no fluoride or thorium; B, $6.4 \times 10^{-3}\text{M}$ $\text{Th}(\text{ClO}_4)_4$. In addition to the $6.41 \times 10^{-3}\text{M}$ thorium perchlorate, perchloric acid and iron III solutions C to F contained various amounts of sodium fluoride as shown C, $2.00 \times 10^{-3}\text{M}$; D, $4.00 \times 10^{-3}\text{M}$; E, $6.00 \times 10^{-3}\text{M}$; F, $1.20 \times 10^{-2}\text{M}$.

that the depression effect is caused by an impurity. The only reasonable explanation for the effect consistent with all the experimental evidence is that it is caused by thorium. No evidence was obtained that contradicts this hypothesis.

It has been concluded as explained above that thorium itself is directly involved in the depression effect. The effect could be explained in one of two ways.

1. Some kind of iron-thorium interaction.
2. An effect of thorium at the electrode surface.

The formation of compounds between highly charged cations, which would strongly repel each other, is virtually unknown. Any bond that did exist between two cations such as iron and thorium would involve the formation of an oxygen bridge or some other type of bridge. In spite of the apparent improbability of such an interaction, some evidence was found for the existence of iron III-thorium complexes at pH values greater than about 2. When the pH of an iron solution is raised by the addition of sodium hydroxide, the iron solution has an obviously lighter color at a given pH if thorium was present prior to the addition of the sodium hydroxide. This effect is shown in Figure 17 (color plate). If thorium is present the precipitation of iron hydroxide does not begin until a higher pH is reached as shown in Figure 18. This figure gives quantitative pH evidence for the existence of iron III-thorium complexes. Hydrolysis curves for

Figure 17. Color plate.

All solutions were 0.05M, $\text{Fe}(\text{NO}_3)_3$. In addition, solutions 2, 3 were 0.05M $\text{Th}(\text{NO}_3)_4$.

Solution 1 had a pH of 1.9 and iron III hydroxide precipitation was imminent. Solution 2 had a pH of 2.0. The lighter color is caused by the thorium present in the solution. Solution 3 and 4 had a pH of 2.6. The thorium present in solution 3 prevented precipitation of iron III hydroxide, as has occurred in solution 4.

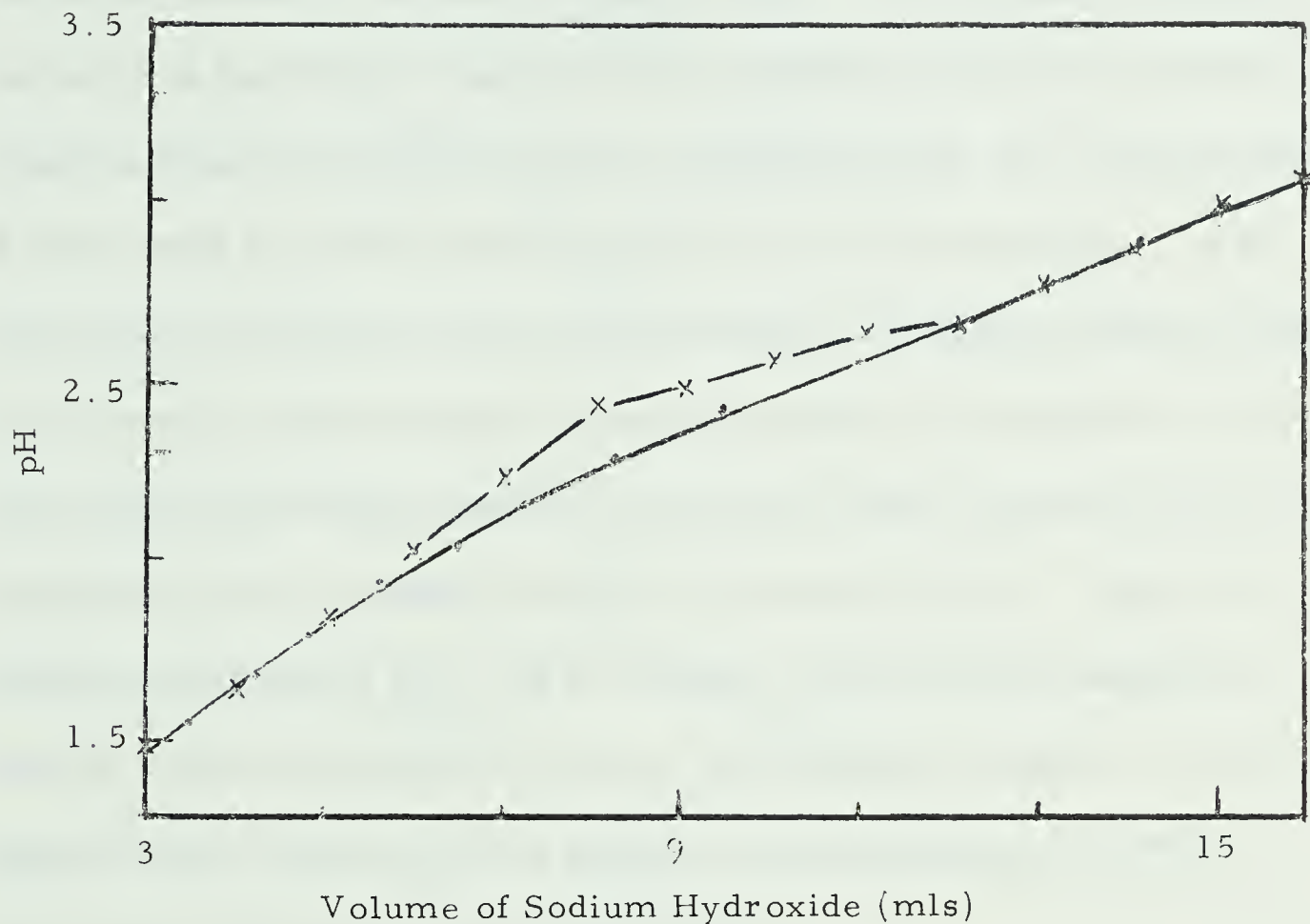


Figure 18. Calculated and experimental hydrolysis curves for a mixture of iron III and thorium. The initial volume of the solution was 50 mls and its composition was, 0.100M, $\text{Fe}(\text{NO}_3)_3$; 0.100M, $\text{Th}(\text{NO}_3)_4$; 0.100M, HClO_4 . The sodium hydroxide solution was 1.015M.

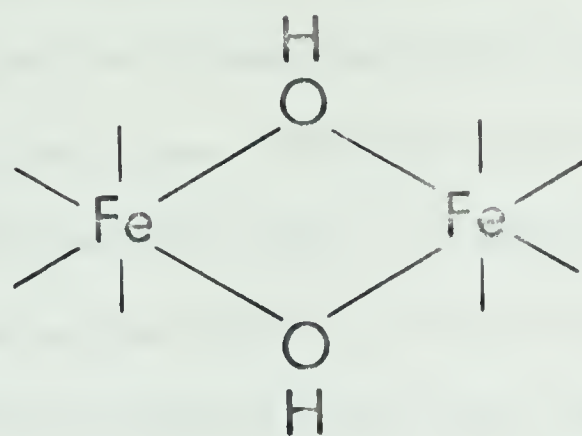
x Experimental

· Calculated

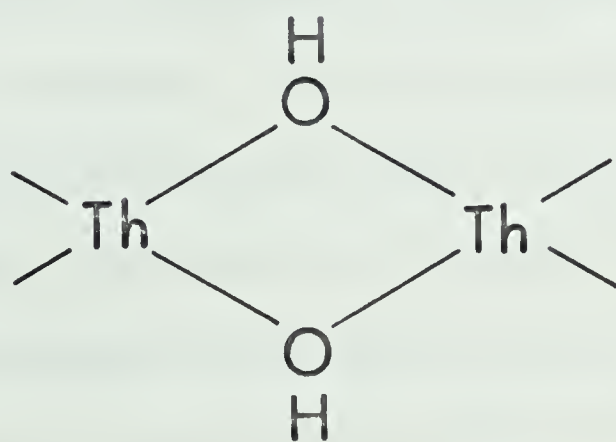
(In the solution containing only iron III precipitation occurred at pH 2.0. In the iron III-thorium solution no precipitation occurred until pH 3.0 was reached.)

iron III perchloric acid and thorium were obtained separately by adding sodium hydroxide to separate solutions and measuring the pH as a function of the amount of sodium hydroxide added. From these individual curves it is possible to construct the composite hydrolysis curve that would be expected for the combined solution of acid, iron, and thorium, if there were no interaction between the iron III and thorium. If the bonds that form between iron III and thorium, through an oxygen bridge, are normally used to connect hydroxyl groups to the metal ions, then less sodium hydroxide should be required to reach a given pH than is indicated by the calculated composite hydrolysis curve. Figure 18 indicates that this is true. For example at pH 2.25 the amount of sodium hydroxide consumed is about 12% less than expected. It is apparent that when thorium is present the precipitation of iron III hydroxide is delayed by about one pH unit.

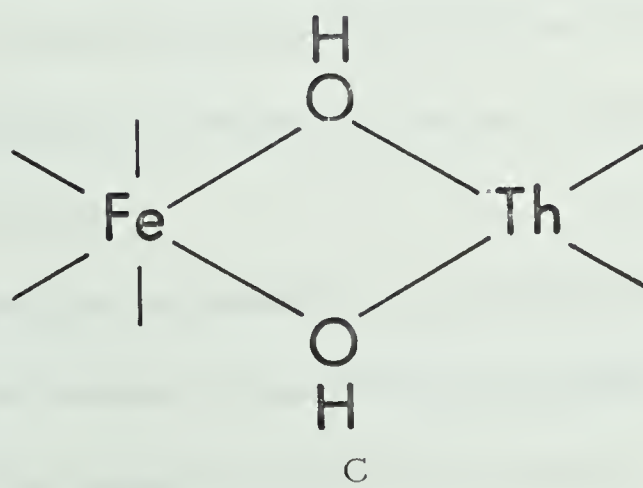
Both iron and thorium form polynuclear hydrolysis complexes (9, 10). It has been suggested (9) that the structure of the iron complex may be as shown in Figure 19A and similarly the thorium complex as shown in Figure 19B . A reasonable possibility for a combined iron III-thorium complex is shown in Figure 19C . Replacing the complexes shown in Figures 19A and 19B with the complex shown in Figure 19C would not lead to the consumption of fewer hydroxyl ions in a composite hydrolysis curve. However mononuclear hydrolysis complexes also co-exist with the polynuclear complexes and replacement



A



B



C

Figure 19

of some mononuclear complexes with a complex similar to that shown in Figure 19C might lead to the results shown in Figure 18 .

In strongly acid solutions iron III has a sharp absorption band in the ultraviolet region. This absorption band is not affected by thorium in 0.1M perchloric acid. In the pH region where thorium affects the color of an iron solution, the iron III absorption band is continuous across the visible and ultraviolet region with no absorption maximum. Because of this fact as well as for other reasons mentioned below, the quantitative investigation of this formation of an iron III-thorium complex is difficult. The ultraviolet absorptivity is much larger than the absorptivity in the visible, so that solutions giving reasonable readings in the visible are too intense in the ultraviolet. The hydrolysis complexes of iron III and thorium both reach equilibrium slowly and this means that the pH of a solution drifts with time. The addition of base to a solution of iron III or thorium produces a local excess of hydrolysis products that are slow to reach equilibrium. Most buffers suitable for the pH region two to three form metal complexes themselves.

If thorium is added to an iron III solution with a pH between two and three the solution does not become lighter in color as one might expect if the thorium and iron III reacted. However, the thorium added would hydrolyze more quickly than it would react with the iron hydrolysis complexes present and a reaction between the

hydrolysis complexes would be slow.

Figures 20 and 21 show spectra for iron III and iron III-thorium solutions. For both the dilute and concentrated solutions the effect of thorium is to decrease absorption in the visible region. In preparing these solutions for spectral measurements, thorium was added prior to increasing the pH with sodium hydroxide. All solutions had the same ionic strength and each pair of solutions had the same pH (± 0.02 pH units). Each solution was allowed to equilibrate for several hours before the spectra were obtained.

If thorium affects the reduction of iron III by forming an iron III-thorium complex, then this effect might also be apparent at the dropping mercury electrode. The reduction wave for iron III at a D.M.E. is masked by the current for the dissolution of mercury so that the actual half wave potential for the reduction of iron III is not accessible. At low pH values (about 1) thorium does not affect the iron III diffusion current. This indicates that the size of the diffusing iron III species does not change measurably when thorium is added to the solution. As the pH becomes higher the iron III hydrolysis products yield almost no reduction current. In any case no significant trend could be detected in the iron III diffusion current as the result of thorium being present.

Complex formation between iron III and thorium should also affect the standard potential of the ferric-ferrous couple. At

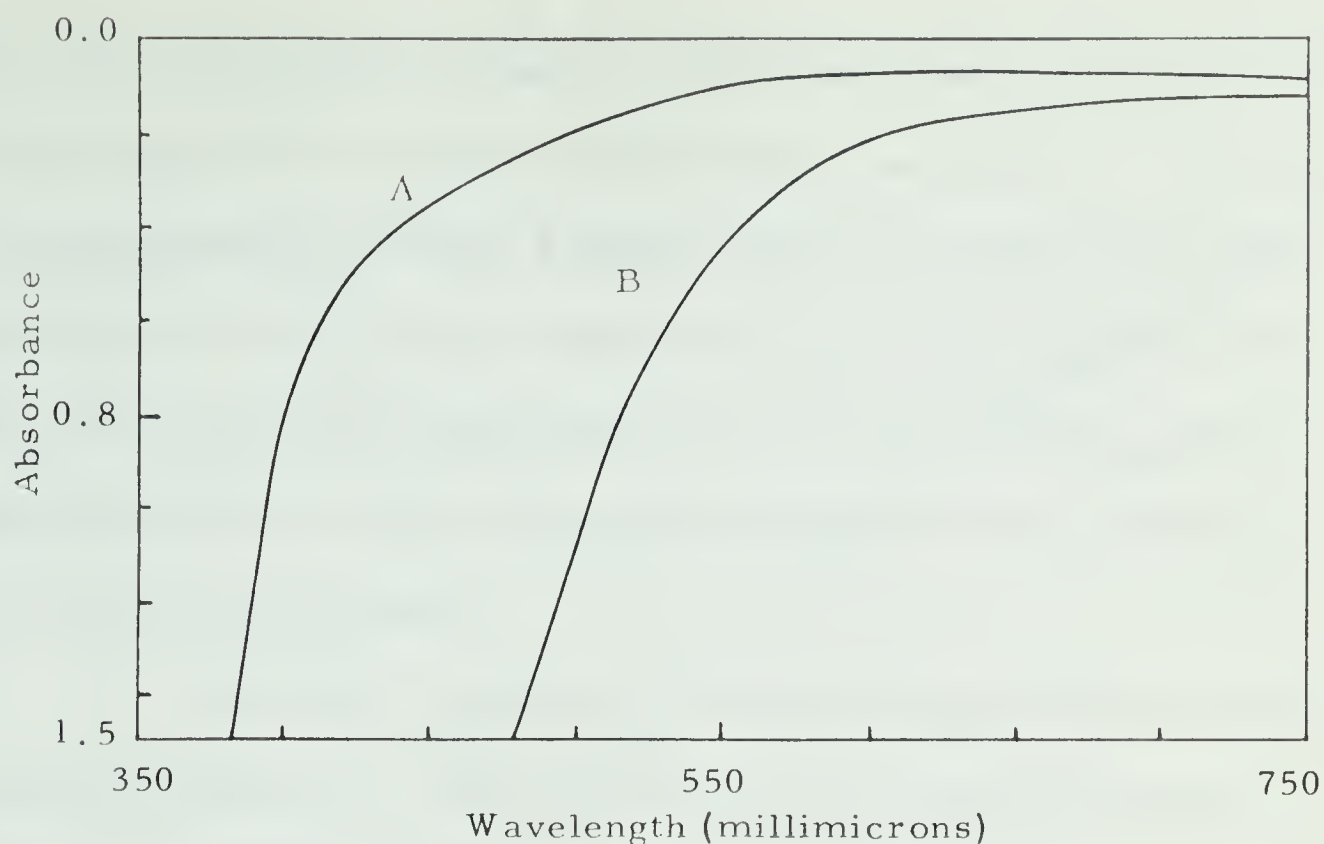


Figure 20. The effect of thorium on the visible spectrum for iron III at pH 2.5. 1cm path length.

A, $9.12 \times 10^{-3} \text{M}$, $\text{Fe}(\text{ClO}_4)_3$; $9.34 \times 10^{-3} \text{M}$, $\text{Th}(\text{ClO}_4)_4$.

B, $9.12 \times 10^{-3} \text{M}$, $\text{Fe}(\text{ClO}_4)_3$.

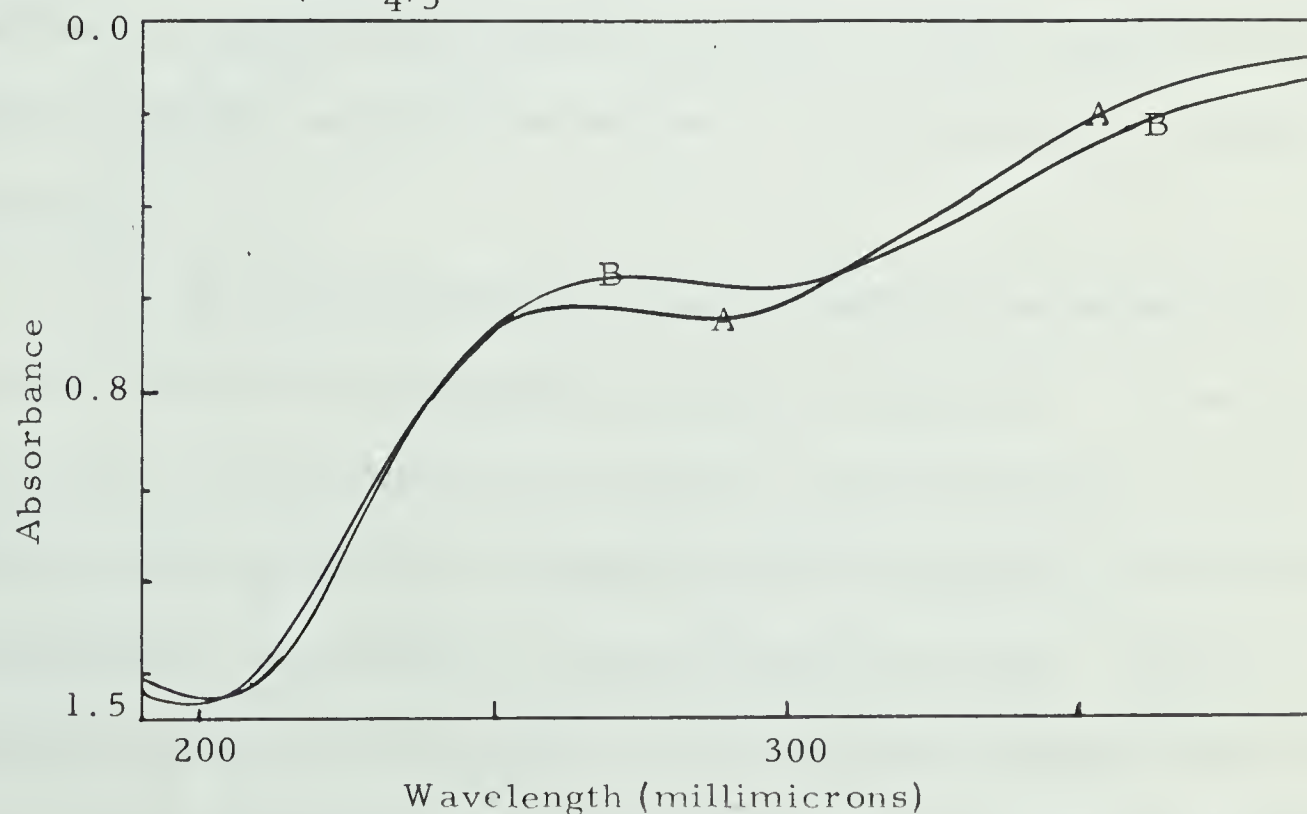


Figure 21. The effect of thorium on the ultraviolet spectrum of iron III at pH 3.0.

A, $3.19 \times 10^{-4} \text{M}$, $\text{Fe}(\text{ClO}_4)_3$; $3.27 \times 10^{-4} \text{M}$, $\text{Th}(\text{ClO}_4)_4$.

B, $3.19 \times 10^{-4} \text{M}$, $\text{Fe}(\text{ClO}_4)_3$.

pH 1 and constant ionic strength no significant change in the potential of the couple could be detected when thorium was present. For example a solution that was 10^{-3}M in $\text{Fe}(\text{ClO}_4)_3$ and 10^{-3}M in $\text{Fe}(\text{ClO}_4)_2$ had a potential of $+0.467 \pm 0.003$ volts (vs S.C.E.). A solution 10^{-3}M in both $\text{Fe}(\text{ClO}_4)_3$ and $\text{Fe}(\text{ClO}_4)_2$ and $3.0 \times 10^{-3}\text{M}$ in $\text{Th}(\text{ClO}_4)_4$ gave an identical potential so that any potential change caused by the thorium was less than 3 millivolts.

The effect of thorium on current voltage curves for iron III is shown in Figure 22. It is interesting to note that the thorium effect is not retained on the electrode. Curve H in Figure 22 was obtained immediately after curve G with the same electrode but a thorium free solution of iron III was used for curve H. This indicates that the effect of thorium cannot be ascribed to tightly adsorbed thorium which would stay on the electrode when it was transferred to a fresh solution.

At a given potential the thorium effect is an exponential function of thorium concentration as shown in Figure 14. If one plots i'/i where i' is the current at any thorium concentration and i is the current when no thorium is present against the logarithm of the thorium concentration, a straight line results (Figures 23 to 26). The absolute values of i'/i for a given set of conditions vary with the nature of the electrode surface, and consequently they are not too reproducible. Moreover the iron current at a given overvoltage tends to decline with

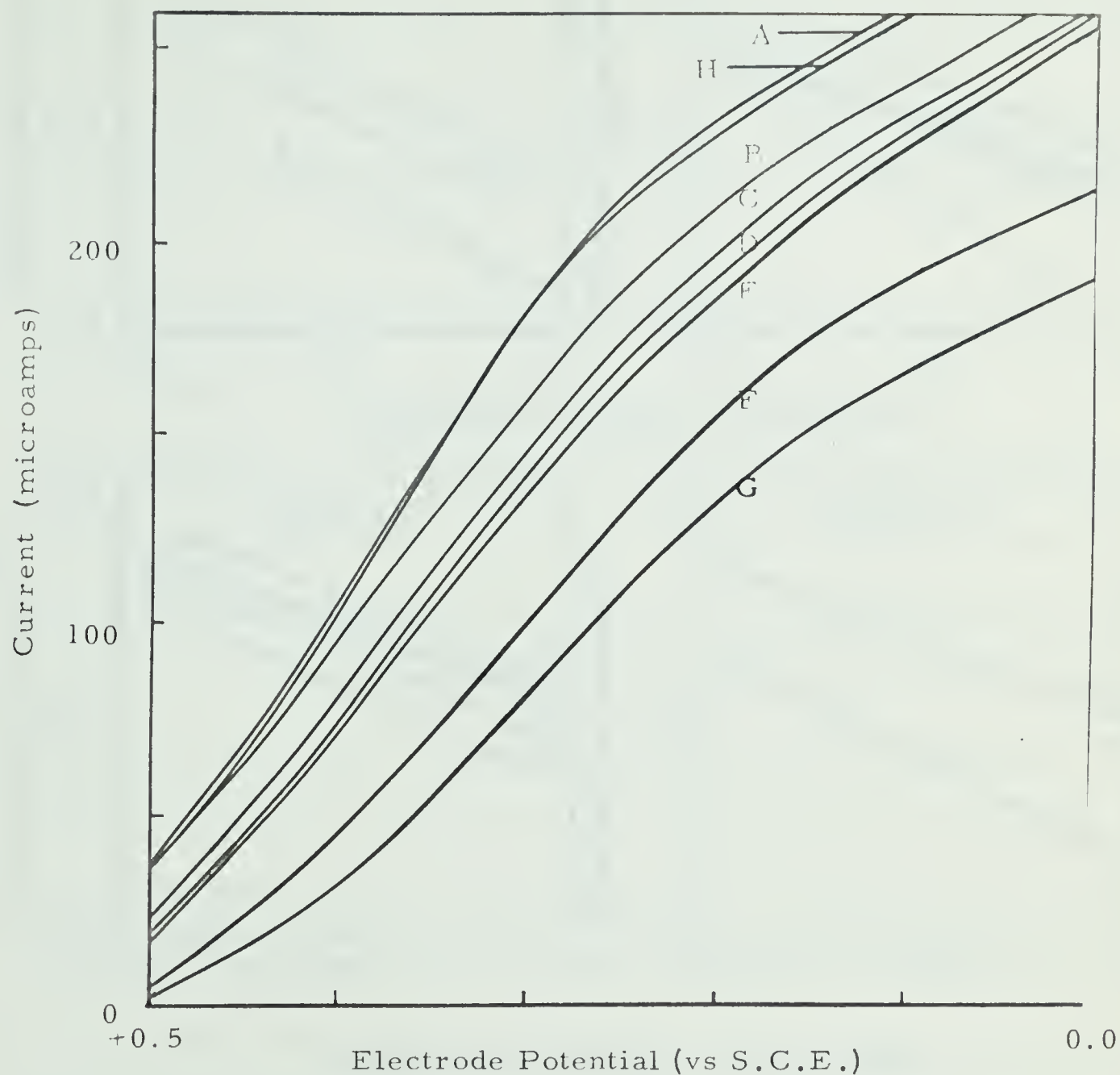


Figure 22. The effect of thorium concentration on current voltage curves for the reduction of iron III at a rotating platinum electrode. All solutions were 0.05M, HClO_4 ; $2.47 \times 10^{-3}\text{M}$, $\text{Fe}(\text{ClO}_4)_3$; A, no thorium; B, $6.17 \times 10^{-4}\text{M}$; C, $1.24 \times 10^{-3}\text{M}$; D, $1.85 \times 10^{-3}\text{M}$; E, $2.47 \times 10^{-3}\text{M}$; F, $1.23 \times 10^{-2}\text{M}$; G, $2.46 \times 10^{-2}\text{M}$. Curve H was obtained immediately after curve G but a fresh thorium free solution with the same composition as for curve A was used.

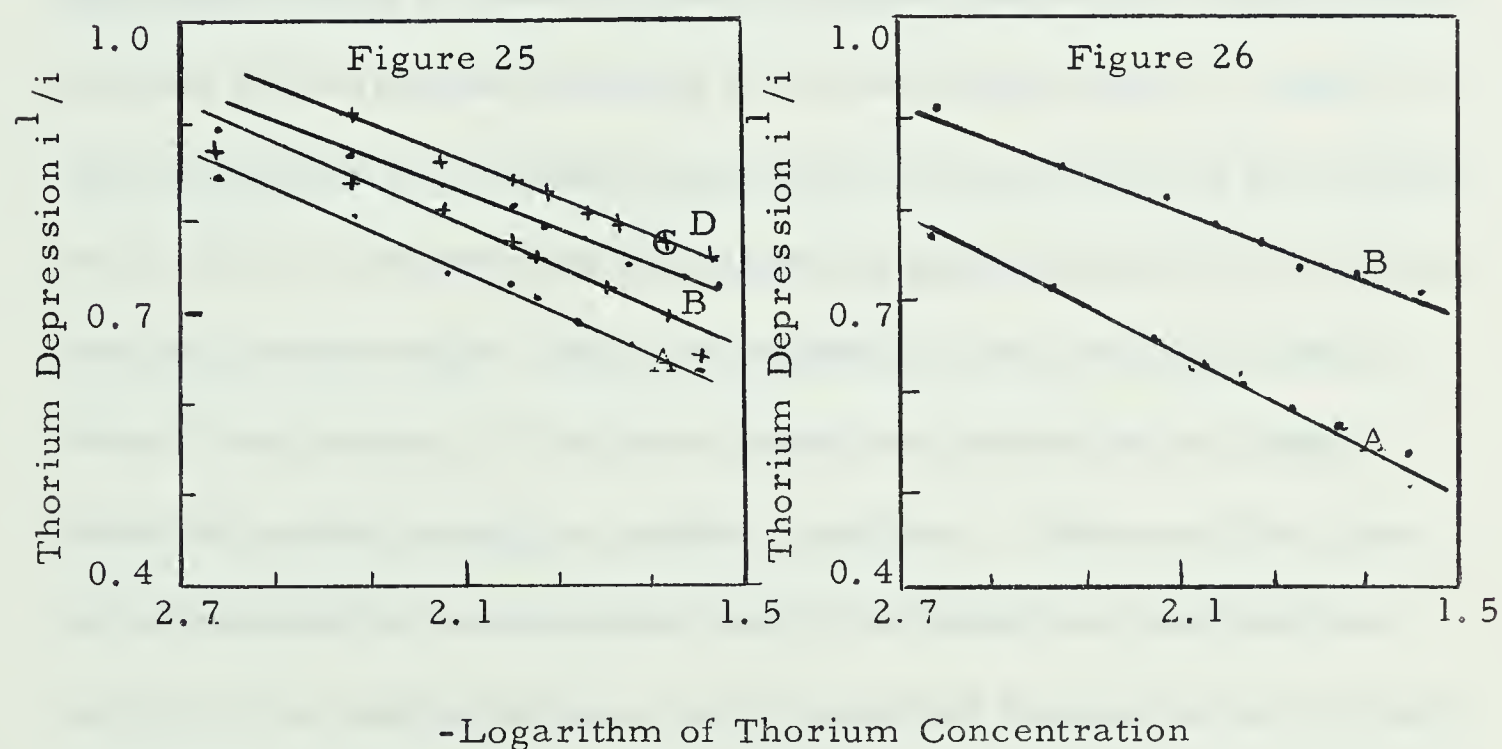
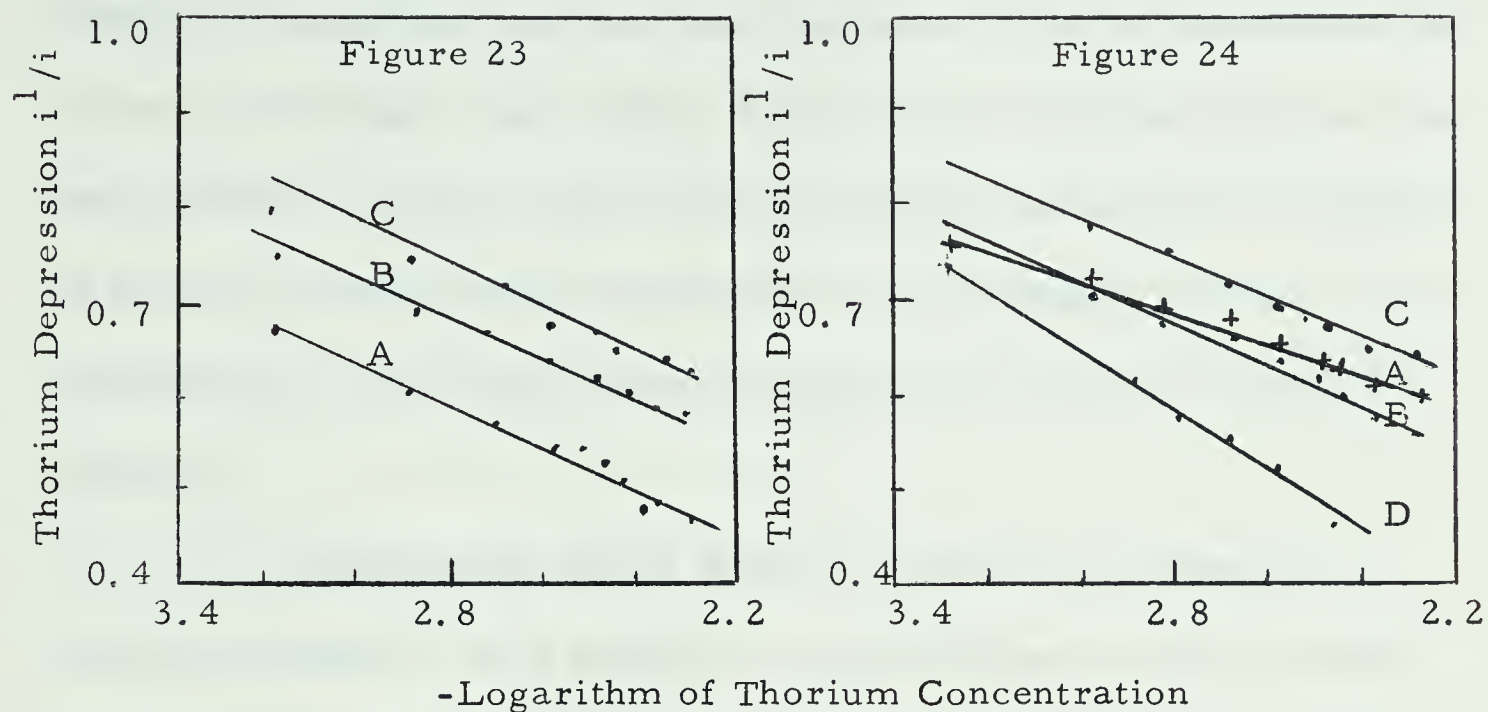


Figure 23. The effect of ionic strength on the thorium depression effect. A 0.1M, HClO_4 ; $1.0 \times 10^{-4}\text{M}$ $\text{Fe}(\text{ClO}_4)_3$; B 1.0M NaClO_4 ; 0.1M, HClO_4 ; $1.0 \times 10^{-4}\text{M}$ $\text{Fe}(\text{ClO}_4)_3$; C 5.0M NaClO_4 ; 0.1M HClO_4 ; $1.0 \times 10^{-4}\text{M}$ $\text{Fe}(\text{ClO}_4)_3$.

Figure 24. The effect of Iron III concentration on the thorium depression effect. All solutions 0.1M HClO_4 , $\text{Fe}(\text{ClO}_4)_3$. A, $1.0 \times 10^{-2}\text{M}$; B, $2.0 \times 10^{-3}\text{M}$; C, $4.0 \times 10^{-4}\text{M}$; D, $1.0 \times 10^{-4}\text{M}$.

Figure 25. The effect of electrode potential (vs S. C. E.) on the thorium depression effect. A, +0.45 volts; B, +0.35 volts; C, +0.25 volts; D, +0.15 volts.

Figure 26. The effect of perchloric acid concentration on the thorium depression effect. A, $1.0 \times 10^{-4}\text{M}$ $\text{Fe}(\text{ClO}_4)_3$; $1.0 \times 10^{-2}\text{M}$ HClO_4 ; B, $1.0 \times 10^{-4}\text{M}$ $\text{Fe}(\text{ClO}_4)_3$; $1.0 \times 10^{-1}\text{M}$ HClO_4 .

time even though all conditions are constant. This is especially true at low overvoltages (up to about 0.2 volts) or if the electrode has just been cleaned. This current decline, which is reduced by the addition of thorium, complicates measurement of the change in current caused by thorium. The trends shown in Figures 23 to 26 are reproducible however.

Exponential curves of this type are not uncommon in electrochemistry. It is possible to speculate that the experimental depression effect is caused by an exponential adsorption isotherm for thorium and a resultant blocking of the electrode surface. Since the rate of reaction is inversely proportional to the fraction of the surface covered, the current would then decrease exponentially with increasing thorium concentration. Such an explanation does not take certain effects into account. It is shown later that thorium is not tightly adsorbed quickly enough to produce the effect. Moreover the effect is not retained on the electrode when it is placed in a thorium free solution; this also eliminates tightly adsorbed thorium as the primary cause of the depression effect.

The data in Figures 23-26 were obtained using an electrode that gave a highly irreversible reduction wave for iron III. The currents measured were a few percent of the estimated diffusion currents. This means that concentration polarization was only a secondary effect at

the electrode surface and that the iron III concentration at the surface of the electrode was essentially constant with changing reduction current. The effects shown in Figures 23-26 can be summarized as follows. The interference of thorium with the reduction of iron III decreases with

- 1) Increasing perchloric acid concentration
- 2) Increasing overpotential
- 3) Increasing ionic strength

The interference shows no significant trend with iron III concentration.

An estimation of the rate at which the thorium effect reaches equilibrium can be obtained by monitoring the iron III reduction current in a well stirred solution and quickly adding a thorium aliquot to the solution. An example of the resulting current-time trace is shown in Figure 27. It is apparent that equilibrium is attained in a second or two. Pipetting and mixing take about this long for completion so the thorium effect may well reach equilibrium more quickly than Figure 27 indicates.

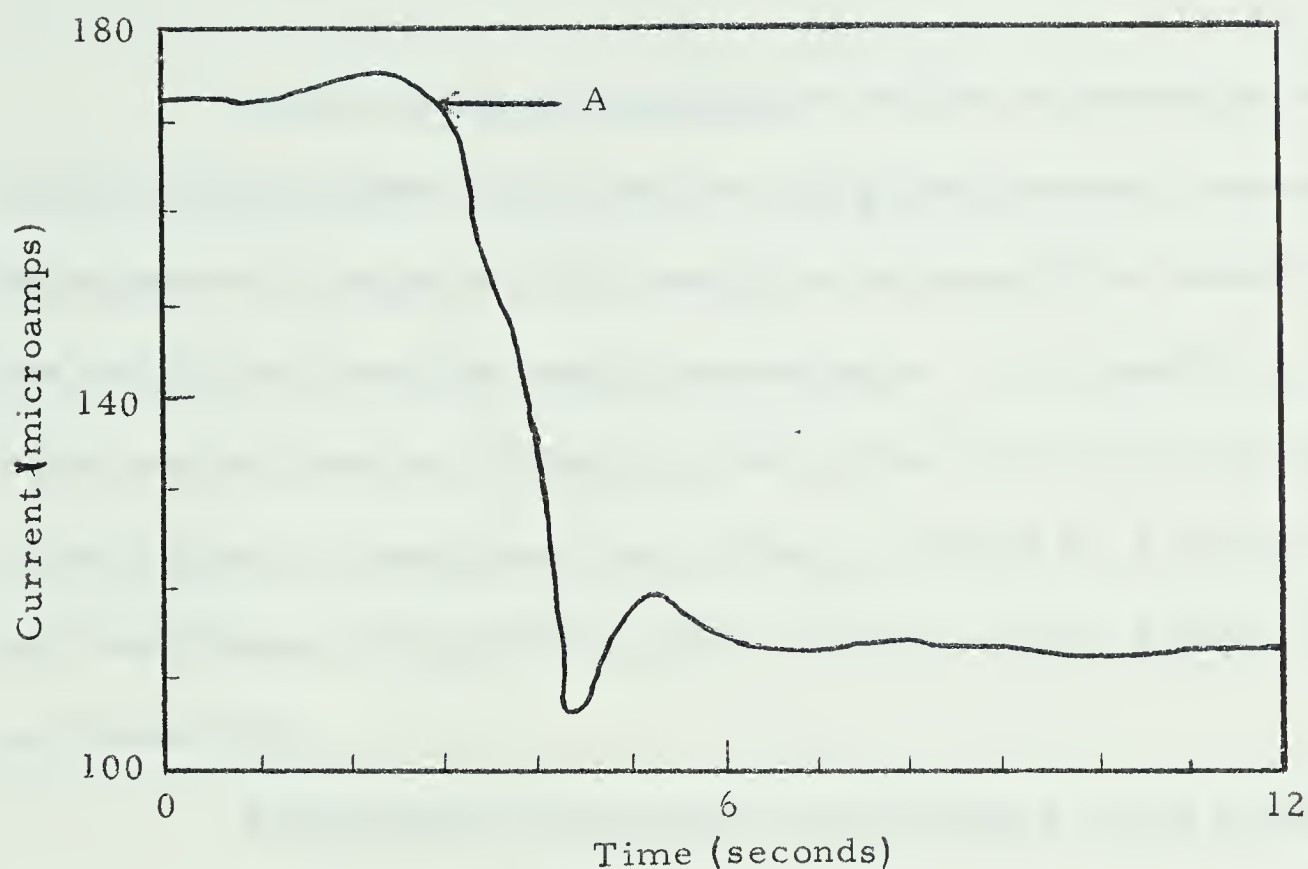


Figure 27. The effect of the addition of a thorium aliquot on a current time trace for the reduction of iron III at $+0.3$ volts (vs S.C.E.) at a rotating platinum electrode. 0.05M , HClO_4 ; $2.47 \times 10^{-3}\text{M}$, $\text{Fe}(\text{ClO}_4)_3$; $1.10 \times 10^{-2}\text{M}$, $\text{Th}(\text{ClO}_4)_4$ added. At point A an aliquot of thorium perchlorate was added to the solution.

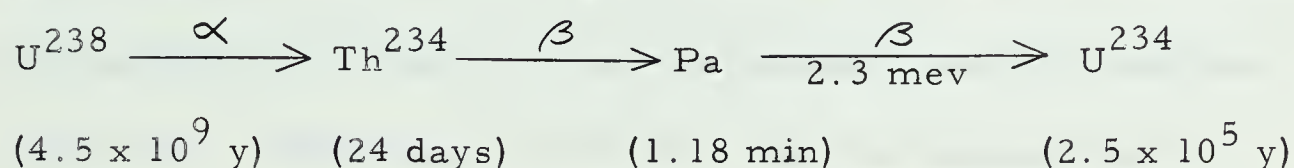
A RADIOCHEMICAL STUDY OF THE ADSORPTION OF THORIUM ON METAL ELECTRODES

For the most part quantitative studies of adsorption on solid metal electrodes have been done using radiochemical techniques. Radiochemistry offers the high sensitivity and specificity needed and the results are therefore usually unambiguous. It is possible to obtain electrochemical evidence for adsorption by the measurement of such things as capacitance and exchange currents but a quantitative and unambiguous interpretation of the results is usually difficult if not impossible.

Radiochemical adsorption measurements can be divided into two general classes; external and in situ. External measurements involve removing the electrode from the solution and washing it prior to counting its radioactivity. This method would detect only strongly adsorbed material that does not wash off. In situ measurements are based on the direct measurement of the change in specific activity of a solution when an electrode is immersed in it. With this (in situ) method of measurement all species in the double layer are considered to be adsorbed. Which of these two methods is chosen depends on the definition of adsorption and the type of electrode under study. In this discussion adsorbed thorium will be defined as that fraction of the thorium that is strongly adsorbed, that is, it is

the thorium that is not easily removed from the electrode by washing.

One isotope of thorium is thorium-234. This isotope has a number of characteristics that make it an attractive choice for adsorption studies. Its decay scheme is



Thorium-234 has a reasonable half-life (24 days). It rapidly attains secular equilibrium with protactinium-234 which has an energetic decay product and a short half-life so that the protactinium decay rate is both proportional to the amount of thorium present and easily counted. Moreover thorium-234 is in secular equilibrium with aged uranium-238 from which it may be easily separated. For these reasons this thorium isotope was used for the adsorption studies.

Quantitative and reproducible radiochemical adsorption studies are not easy. For several reasons the results reported here should be regarded as only semi-quantitative.

In the separation procedure used, thorium-234 had to be isolated from large quantities of 9.6M hydrochloric acid which contained traces of ion exchange resin. The hydrochloric acid was evaporated to dryness. Then the residue was heated with perchloric acid to remove the traces of resin. Undue heating made it difficult to again bring the thorium-234 into solution. Non-volatile contaminants in the hydrochloric acid remained with the thorium. The

difficulties of preparing a platinum surface with reproducible adsorption characteristics are substantial. To avoid cumbersome radiation protection procedures small quantities of thorium were used. This meant that the count rates obtained, for adsorption measurements, were seldom more than a few percent greater than the background count rate. These facts and the fact that the measurements are based on nominal electrode areas rather than true electrode areas, should be kept in mind when interpreting the data. In the external method used for this study, loosely adsorbed thorium was removed by washing while thorium in microcracks in the electrode would give the appearance of being adsorbed.

Two types of platinum electrodes were used in this study. One electrode consisted of a platinum wire electrode sealed in a soft glass tube such as was used for amperometric titrations. To use this electrode for adsorption studies the thorium adsorbed on the electrode was stripped into a small volume of warm nitric acid and this nitric acid was analyzed for thorium-234 as described later. Adsorption on a palladium wire electrode was studied similarly.

The second platinum electrode used consisted of a smooth platinum foil disc (diameter 2 cm, 0.1 mm thick) cemented to a glass tube with silicon rubber cement in such a way that almost no cement was exposed to the thorium solution. The glass tube contained a drop of mercury and a copper wire to make electrical contact (Figure 29).

The increased area of this electrode, compared to the wire electrode, meant that the electrode could be counted directly without stripping the adsorbed thorium.

Two methods of separating thorium-234 from uranium were used. The first method was that of Sill (36) which utilizes an anionic exchange resin for the separation. The uranium-thorium mixture is added to the ion exchange column in 9.6M hydrochloric acid. The anionic uranium chloride complexes, which exist in this medium, are retained by the resin while thorium passes through the column. It is important to precondition the column with hydrochloric acid to reduce the amount of organic matter leached from the resin. The hydrochloric acid effluent was then evaporated to dryness on a hot plate at low heat. A few drops of perchloric acid were then added and this solution was heated to dryness to remove organic matter. Finally the thorium-234 was dissolved in a few drops of 1M perchloric acid for later use.

The second method of separating thorium from uranium was based on the fact that iron III hydroxide is an efficient scavenger for thorium. A few milligrams of ferric nitrate are added to a solution of uranyl nitrate. Ammonium carbonate was then added to the solution till the yellow uranium precipitate that formed dissolved leaving only the brown iron III hydroxide precipitate. The iron hydroxide was allowed to settle and was filtered with a glass filter mat using the device shown

in Figure 28 . The glass mat was treated with a few drops of 9.6M hydrochloric acid and the resulting solution of iron III and thorium was passed through a small anion exchange column using 9.6M hydrochloric acid as an eluant. The iron III remained on the column, presumably in the form of anionic chloride complexes. The effluent was evaporated to dryness and treated with perchloric acid as described previously. This procedure has the advantages of not requiring large amounts of hydrochloric acid or a large ion exchange column.

Thorium-234 solutions were standardized according to the following procedure (24). Separate weighed portions (about 0.01 ml) of the unknown thorium-234 solution were added to 50 ml beakers which contained 10 mls of 0.1M nitric acid. Three ten ml portions of a standard uranium solution (0.1M HNO_3 , $8 \times 10^{-3}\text{M UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were pipetted into 50 ml beakers. Three drops of 0.1M ferric nitrate were added to each 50 ml beaker. The solutions were then warmed to about 60°C and 0.5M ammonium carbonate was added to both unknowns and standards, until only an iron III hydroxide precipitate remained. A yellow uranium precipitate formed in the uranium standards but redissolved upon the addition of more ammonium carbonate. All solutions were kept at about the same stage of iron III hydroxide precipitation at any given time. The solutions, containing the precipitate, were cooled and the iron III hydroxide precipitate (which contained adsorbed thorium) was filtered with a glass filter mat as shown in

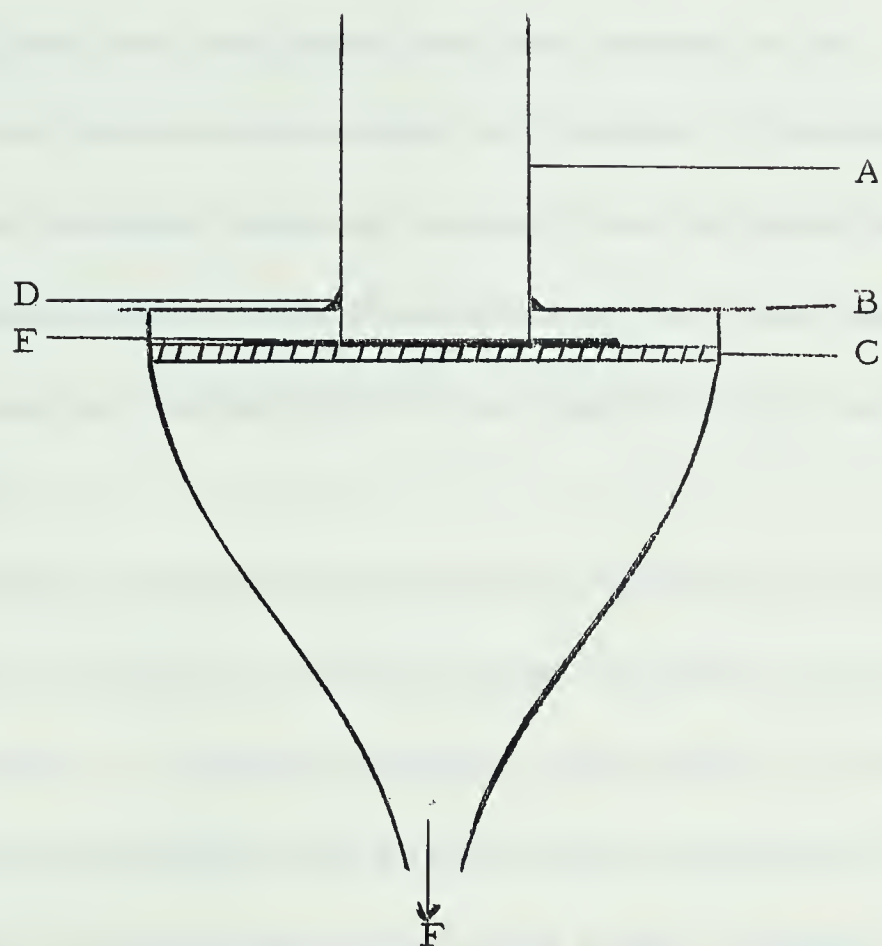


Figure 28. A device for filtering iron III hydroxide onto a glass filter mat. A, 10 mm OD glass tube; B, thin flexible rubber sheet; C, porous glass frit; D, silicon rubber cement; E, glass filter mat; F, to filter flask. Drawn to a scale of twice actual size.

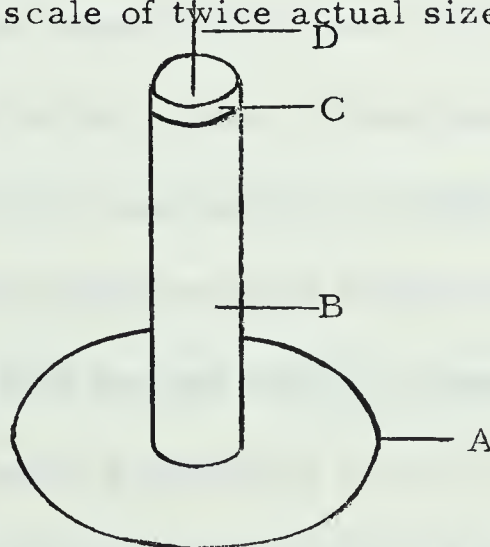


Figure 29. Platinum disc electrode. A, platinum disc; B, mercury in glass tube; C, silicon rubber cement; D, Cu wire.

Figure 28. One drop of an acetone solution of collodion was placed on the precipitate and the precipitate was then allowed to dry. Finally the glass mats were placed in planchets and counted. The amount of thorium-234 in the standard uranium solution was calculated and the ratio of the unknown count rate to standard count rate was used to calculate the amount of thorium-234 in the original weighed aliquot of unknown solution.

To measure thorium adsorption the electrode was placed in a small volume of solution containing known amounts of thorium-234 and ordinary thorium. After the elapse of a specified time the electrode was removed from the solution and washed with distilled water for 30 seconds. Then the adsorbed thorium was either stripped with nitric acid or the electrode was counted directly and the amount of adsorbed thorium was calculated from the count rate. The counting geometry of the foil electrode was determined as follows. The electrode was counted. A portion of the thorium-234 adsorbed on the electrode was stripped with nitric acid. Then the electrode was recounted and the nitric acid was analysed for thorium-234. Analysis of the nitric acid solution indicated how much thorium had been removed and this information coupled with the percentage change in the electrode's activity gave a counting geometry of 15%. When the thorium was stripped with nitric acid the nitric acid solution was analysed for thorium-234 as outlined previously using thorium

standards for comparison.

The potential of the electrode with respect to a S.C.E. reference electrode was controlled with the Metrohm Polarecord.

These procedures were far from ideal. Stripping the electrode with nitric acid alters its surface and the products of the reaction between nitric acid and platinum are left on the platinum surface (7). Removing the platinum disc electrode and allowing it to dry while counting would also produce changes in the electrode surface.

OBSERVATIONS

When the platinum foil electrode was immersed in a 0.00327M thorium perchlorate solution at pH 1.5 (HClO_4) and at a potential of +0.30 volts for ten minutes the amount of adsorbed thorium was 2×10^{-10} moles/cm². After reimmersion in this solution for fifteen minutes the amount of adsorbed thorium was 3×10^{-10} moles/cm².

The electrode was cleaned in warm nitric acid and conditioned at 0 volts (vs S.C.E.) for several minutes until the background current declined to a few microamps. This cleaning and conditioning process was adopted to help remove nitric acid residues from the surface.

Repeating this immersion with a clean electrode at 0.0 volts (vs S.C.E.) for fifteen minutes gave an amount of adsorbed thorium

of 9×10^{-11} moles/cm². Reimmersion in the solution for another fifteen minutes did not change the amount of adsorbed thorium.

After cleaning the electrode and immersing it in the same solution at +0.3 volts (vs S.C.E.) the amount of adsorbed thorium was 1.0×10^{-10} moles/cm². Reimmersion for fifteen minutes did not change this value. The amounts of thorium adsorbed, after cleaning, in a second set of immersions was 6×10^{-11} moles/cm² and 7×10^{-11} moles/cm².

After fifteen minute immersions and cleaning the amounts of adsorbed thorium were both 1×10^{-11} moles/cm² at +1.0 volts (vs S.C.E.) and -0.5 volts (vs S.C.E.).

The effect of electrode potential was also studied using a platinum wire electrode. Ten minute immersions in 0.00106M thorium perchlorate at pH 2.5 were used. The electrode was cleaned as outlined previously. The amounts of thorium adsorbed on the electrode at various potentials were as follows: 0.0 volts (vs S.C.E.), 1×10^{-10} moles/cm²; 0.5 volts (vs S.C.E.), 1×10^{-9} moles/cm²; 1.0 volts (vs S.C.E.), 2×10^{-10} moles/cm².

Using a palladium wire electrode and one minute immersions in a 0.0016M thorium perchlorate solution 0.05M in perchloric acid at a potential of +0.5 volts (vs S.C.E.) an average value of $1 \pm 0.3 \times 10^{-11}$ mole/cm was obtained from four determinations.

These results bring out two interesting facts about the adsorption of thorium on solid metal electrodes. First, strong adsorption of thorium does occur on platinum and palladium electrodes at potentials substantially more positive than the potential of null charge. Secondly, such adsorption is slow and requires several minutes to reach equilibrium. In general immersion times shorter than a few minutes were not used because experimental conditions were such that the amount of adsorption occurring in much shorter times could not be measured. One minute adsorption times were used with the palladium electrode but a higher ratio of thorium -234 to ordinary thorium was used than for other experiments and the amount of thorium adsorbed was an order of magnitude less than for platinum electrodes with longer immersion times.

The values for adsorption reported here agree reasonably well with those reported by Balashova and Merkulova (3) who studied the adsorption of several anions and cations on platinum by radiochemical techniques. For the adsorption of cesium they report 2×10^{-12} moles/cm² at +0.5 volts (vs S. C. E.) in 0.01 molar cesium sulfate at pH 2.5. These authors did not indicate whether an external or in situ method of analysis was used nor did they indicate the time allowed for equilibration prior to measurement.

If we have 10^{-10} moles of thorium adsorbed per cm² of platinum the area available for each adsorbed atom is 160 square

Angstroms. The area occupied by a hydrated adsorbed thorium atom is difficult to estimate but one would expect it to be less than 160 square Angstroms. Moreover the true surface area is substantially larger than the geometric area and this would increase the available area per adsorbed thorium atom. Therefore the amount of adsorbed thorium on the platinum electrode was substantially less than a monolayer.

Because of the amount of time required for thorium adsorption to reach equilibrium it appears that tightly adsorbed thorium is not primarily responsible for the effect of thorium on the reduction of iron III. The type of adsorption demonstrated in this section reaches equilibrium only after several minutes whereas the effect of thorium on the reduction of iron III reaches equilibrium in a second or two. This view is supported by the fact that the thorium effect could not be transferred on an electrode from a thorium solution of iron III and thorium to a thorium free solution of iron III, even though radiochemical studies showed that most adsorbed thorium was still retained on an electrode after the electrode had been in distilled water for an hour.

THE EFFECT OF THORIUM ON THE CHRONOPOTENTIOMETRY
OF IRON III

At rotating metal electrodes (with the exception of the smooth rotating metal disc electrode) diffusion conditions are not well defined. The current flowing through the electrode depends on its speed of rotation, and its configuration, as well as its potential. If the current is diffusion controlled the concentration of reactant at the electrode surface is essentially zero. However over a large part of the current voltage curve for an irreversible reaction the current is partly kinetically controlled and partly diffusion controlled. Consequently for an irreversible reaction the concentration of reactant at the electrode surface is poorly defined.

Chronopotentiometry consists of forcing a constant current through an electrode and recording the electrode potential as a function of time. When the concentration of reactant at the electrode surface decreases toward zero the electrode potential changes markedly. When the potential has changed sufficiently another reaction begins to occur and the potential is stabilized. In this technique diffusion conditions are well defined, and given certain conditions it is possible to analyse an irreversible chronopotentiogram to obtain a rate constant for the electrode reaction and the transfer coefficient. The transfer coefficient from a simplified point of view, is the fraction of the

electrode potential used to increase the rate of the forward electrode reaction.

In chronopotentiometry the transition time τ is defined as the time required for the concentration of reactant at the electrode surface to reach zero. It has been theoretically shown that

$$\tau^{1/2} = \frac{\pi^{1/2} n F C A D^{1/2}}{2i} \quad (1)$$

τ = Transition time (seconds)

n = Faradays per molar unit of reaction

A = Electrode area (cm^2)

F = Faraday (96,493 coulombs)

D = Diffusion coefficient (cm^2/sec)

C = Concentration (moles/ cm^3)

i = Current (amps)

$\pi = 3.1416$

This equation holds regardless of the reversibility or irreversibility of the electrode reaction.

For an irreversible (slow) system the current forced through the electrode may be equated to the rate of reaction at the electrode. Under these conditions Delahay has shown (19) that the electrode potential E , with respect to a reference electrode, is given by the expression

$$E = \frac{RT}{\alpha nF} \ln \frac{nFCk}{i_A} + \frac{RT}{\alpha nF} \ln (1 - (\frac{t}{\tau})^{1/2}) \quad (2)$$

t = Time elapsed (seconds)

k = The rate constant for the electrode reaction at the potential of the reference electrode ($\text{sec}^{-1}\text{cm}^{-2}$)

α = Transfer coefficient

i_A = Current density (amps/cm^2)

R = Gas constant

T = Absolute temperature

By rearranging this equation we obtain

$$\ln (1 - (\frac{t}{\tau})^{1/2}) = \frac{\alpha nF}{RT} E - \ln \left(\frac{nFCk}{i_A} \right)$$

If $\ln (1 - (\frac{t}{\tau})^{1/2})$ is plotted against E a straight line with slope $\frac{\alpha nF}{RT}$ and intercept $-\ln \left(\frac{nFCk}{i} \right)$ should result.

Equation (2) is valid if the chronopotentiogram is obtained from an irreversible electrode reaction. For an irreversible reaction the backward rate of reaction can be neglected in comparison to the forward rate of reaction. Because the rate of reaction at an electrode is an exponential function of potential this irreversibility condition is met by an overvoltage of 0.1 volt or greater (19). Equations (1) and (2) both assume linear diffusion to the electrode surface and the absence of stirring and convection.

The major difficulty with irreversible chronopotentiometry, especially at solid metal electrodes, lies in the fact that although

the transition time is well defined in theory, the choice of a method of its experimental measurement is arbitrary. This is especially true if the chronopotentiogram is so irreversible that the transition time is not well defined experimentally. Several methods of measuring the transition time have been proposed for irreversible chronopotentiograms (19, 32, 34) but the proposed methods are essentially empirical. Figure 30 shows plots of $1 - (t/\tau)^{1/2}$ on a logarithmic scale against the electrode potential for three values of the transition time as obtained from three different methods of measuring it from the same chronopotentiogram. It is apparent that the method of measuring the transition time ascribed to Kuwana gives the most nearly linear plots and for this reason Kuwana's method of measuring the transition time was used. This method was also recommended by Russell and Petersen (34) who studied the irreversible reduction of iodate at a mercury electrode.

The method of measuring the transition time ascribed to Kuwana is shown in Figure 31. The transition time is taken as the time when the chronopotentiogram becomes linear. Because the chronopotentiogram approaches linearity asymptotically it might seem that it would be difficult to fix the time when the chronopotentiogram becomes linear. However by superimposing the edge of a transparent triangle on the chronopotentiogram the choice of the correct value for the transition time can be accomplished with little error.

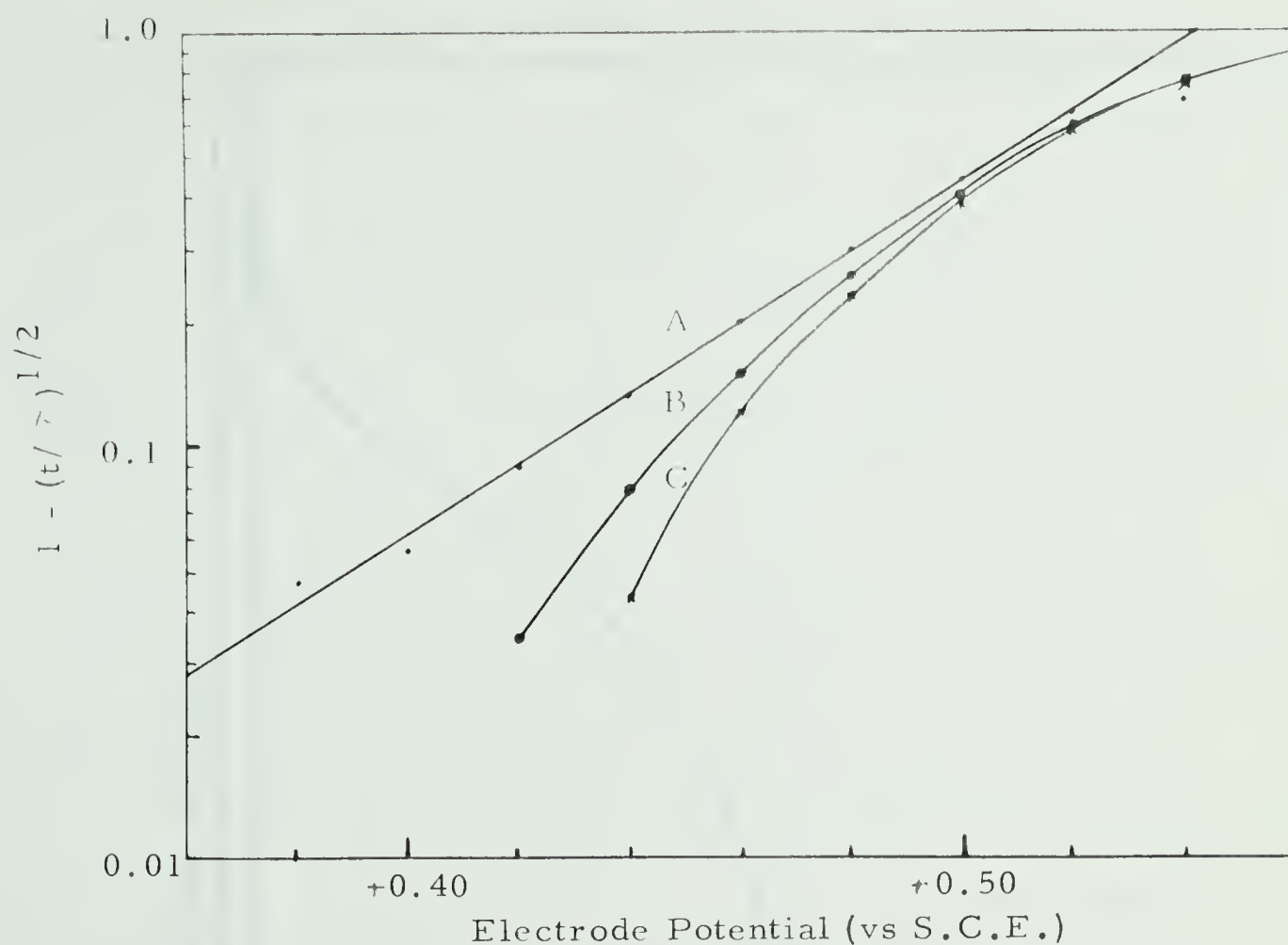


Figure 30 The relation between $1 - (t/\tau)^{1/2}$ and the electrode potential for transition times as measured according to several authors. A platinum wire electrode and nominal current density of 300 amp/cm^2 were used.

A, Transition time 10.5 seconds according to Kuwana (34).

B, Transition time 9.28 seconds according to Reinmuth (32).

C, Transition time 8.66 seconds according to Delahay (19).

$3.28 \times 10^{-3} \text{M}$, $\text{Fe}(\text{ClO}_4)_3$; $1.23 \times 10^{-2} \text{M}$, $\text{Th}(\text{ClO}_4)_4$; 0.10M , HClO_4 .

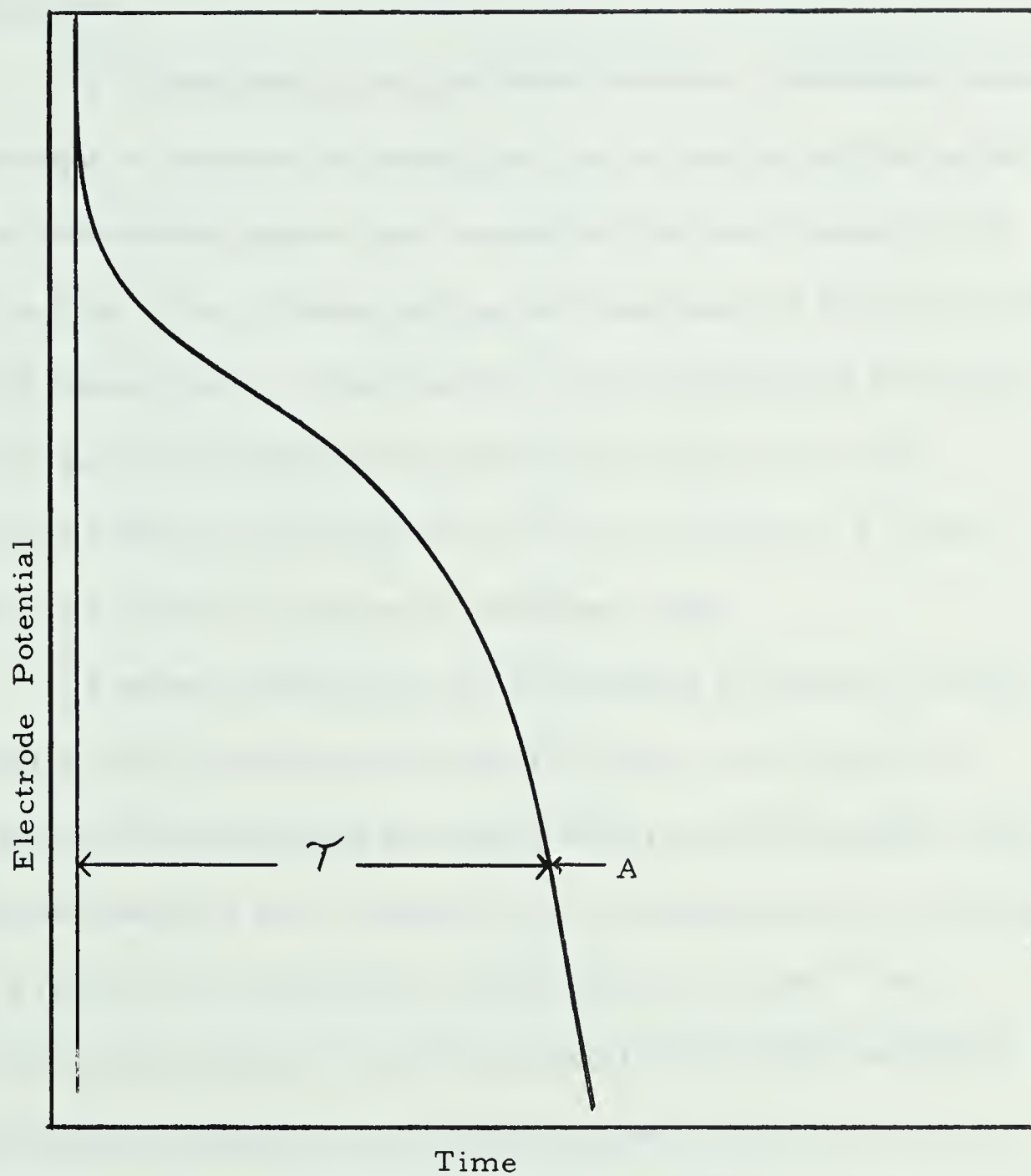


Figure 31. Measurement of the transition time (τ) according to Kuwana (34). At point A the chronopotentiogram becomes linear.

This is the case because when the chronopotentiogram is reasonably steep an error on the potential axis produces a small error in the transition time.

A recent publication has shown that for a reversible system it is possible to measure the transition time by electrically differentiating a chronopotentiogram, and measuring the time elapsed to the inflection point of the chronopotentiogram (maximum of the differential curve)(31). Measuring the transition time to the beginning of the linear portion of an irreversible chronopotentiogram agrees with this differential method to the extent that the linear portion of a chronopotentiogram is also the region of maximum slope.

Further evidence for the correctness of Kuwana's method of transition time measurement is the fact that, even though the shape of the chronopotentiogram varied widely, and decreasing values of the transition time were obtained with increasing thorium concentration at a fixed iron concentration, linear plots of $1-(t/\tau)^{1/2}$ on a logarithmic scale against electrode potential were always obtained provided that the transition time was measured as described above.

If the method of measuring the transition time is correctly chosen then according to Equation 1 the product $i\tau^{1/2}$ should be constant as the current is changed. Table 6 shows the values of $i\tau^{1/2}$ for the three different methods of measuring the transition time as for Figure 30. It is apparent from this table that $i\tau^{1/2}$

TABLE 6. THE DEPENDENCE OF THE PRODUCT $i\tau^{1/2}$ ON i

i μamp	$i\tau^{1/2}$ $\mu\text{amp sec}^{1/2}$	$i\tau^{1/2}$ $\mu\text{amp sec}^{1/2}$	$i\tau^{1/2}$ $\mu\text{amp sec}^{1/2}$
	A	B	C
15.4	89.5	94.3	105.0
18.4	87.9	91.8	100.3
21.7	81.8	85.5	92.6
25.2	83.5	87.5	95.8
27.2	84.1	87.6	95.0
29.6	82.6	86.5	93.8
32.1	81.0	85.2	91.5
36.3	80.9	85.2	91.6
46.6	81.2	84.0	90.3
median	82.6	86.5	93.8

A Transition time measured according to (19).

B Transition time measured according to (32).

C Transition time measured according to (34).

$\text{Fe}(\text{ClO}_4)_3$, $3.28 \times 10^{-3}\text{M}$; $\text{Th}(\text{ClO}_4)_4$, $1.23 \times 10^{-2}\text{M}$; HClO_4 , 0.1M .

Platinum wire electrode 0.1 cm^2 nominal surface area.

is equally constant for all three methods of measuring the transition time and therefore from this point of view there is no reason to prefer one method over another despite the fact that values for the transition time are significantly different.

The fact that $i\gamma^{1/2}$ is constant for any one method also indicates that the electrode reaction is not preceded by a slow chemical step. However experimental conditions for Table 6 are such that only an extraordinarily slow chemical step would be detected. In any case a slow preceding chemical step is improbable for the reduction of iron III.

Figure 32 shows a series of chronopotentiograms for the reduction of iron III with various amounts of thorium. There are several features of these curves that are significant. First the overvoltage increases steadily with increasing thorium concentration. Secondly the shape of the chronopotentiogram is changed when thorium is added. Finally transition time decreases as the thorium concentration increases.

Both the change in shape and the increasing overvoltage are characteristic of irreversible chronopotentiograms. However according to Equation (1) the transition time is independent of the reversibility of a chronopotentiogram. It has been suggested that adsorption of an inactive species could shorten the transition time by reducing the amount of electrode surface that is available for the

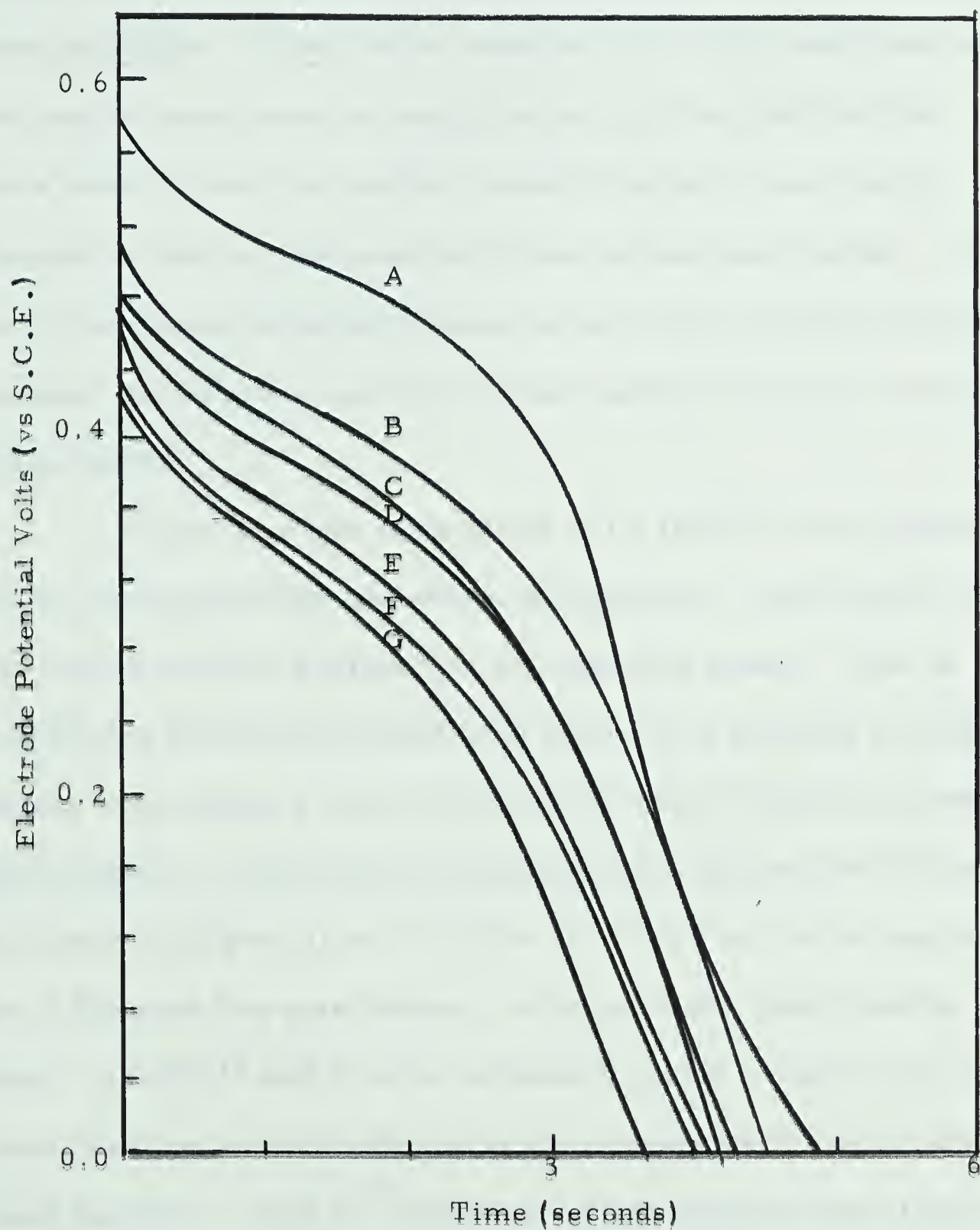


Figure 32. Chronopotentiograms for the reduction of ferric perchlorate at a platinum electrode with various concentrations of thorium perchlorate. $3.28 \times 10^{-3} \text{M}$, $\text{Fe}(\text{ClO}_4)_3$; 1.0M , HClO_4 . Nominal current density 300 amp/cm^2 . A, 0; B, $1.64 \times 10^{-4} \text{M}$; C, $3.27 \times 10^{-3} \text{M}$; D, $6.54 \times 10^{-3} \text{M}$; E, $1.64 \times 10^{-2} \text{M}$; F, $3.27 \times 10^{-2} \text{M}$; G, $9.80 \times 10^{-2} \text{M}$.

reaction 13. Consequently, at a fixed concentration of reactant, the transition time must decrease because all the other terms in Equation 1 remain unchanged. Some caution must be used in this interpretation. If the reaction under study is highly irreversible the electrode can attain a potential such that another reaction begins to occur before the transition time for the reaction of interest has been reached. Under these circumstances an effect similar to that shown in Figure 32 would be obtained but the transition time for the reaction of interest would not be measurable.

Figure 33 shows the relation of $1 - (t/\tau)^{1/2}$ to the potential E for the chronopotentiograms shown in Figure 32. The relation is linear when thorium is present, but not when it is absent. This is not surprising because the reduction of iron III at a platinum electrode is usually regarded as a fairly reversible process to which Equation 2 would not apply. The actual overvoltage for the thorium free chronopotentiogram in Figure 32 is 0.08 volts at $t = 1/2\tau$ so that the applicability of Equation 2 is questionable. A more nearly linear relation between $1 - (t/\tau)^{1/2}$ and E can be obtained by using a smaller value but even then the linearity obtained is not comparable to that for the relation between $1 - (t/\tau)^{1/2}$ and the electrode potential when thorium is present. So it would seem that Equation 2 cannot be used to obtain the transfer coefficient when thorium is not present.

The nearly parallel lines of Figure 33 indicate that the

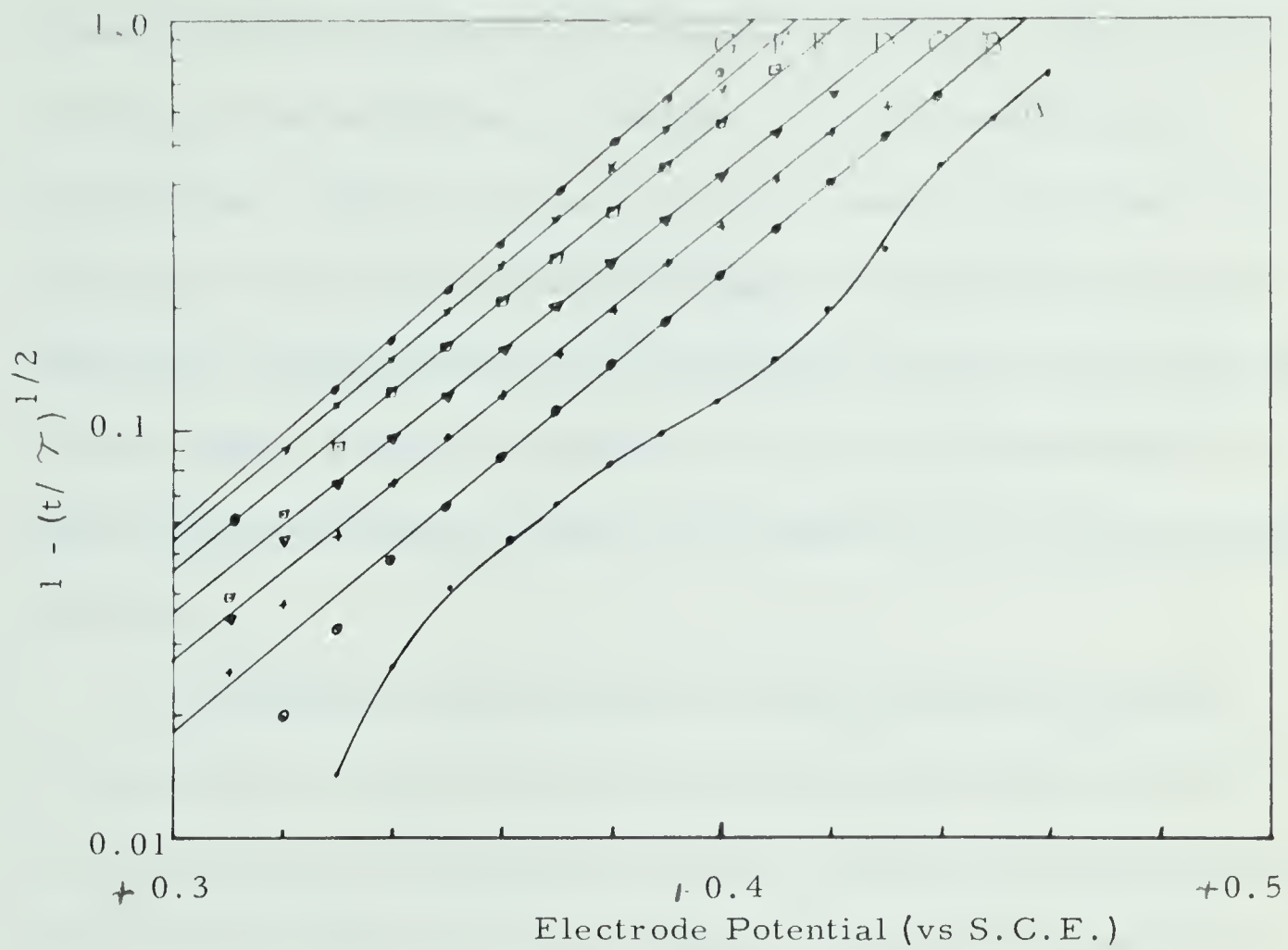


Figure 33. The relation between $1 - (t/\tau)^{1/2}$ and the electrode potential for the chronopotentiograms in Figure 32 .

transfer coefficient is constant with changing thorium concentration.

It is difficult to understand how the introduction of a small amount of thorium would alter the transfer coefficient, if the transfer coefficient remains constant, thereafter, with increasing thorium concentration. However the current pulse measurements discussed later indicate that this may be what happens. Because the transfer coefficient is constant with increasing thorium concentration (Table 7) while the rate of reaction continues to decline it is apparent that the major effect of thorium is on the rate of reaction rather than the transfer coefficient.

It should also be possible to study the effect of thorium on the oxidation of iron II but chronopotentiograms for this oxidation are poorly defined in comparison with the reduction of iron III because oxidation of the electrode surface begins at potentials not much more positive than the standard electrode potential for the ferric-ferrous couple. Therefore it was not possible to measure transition times for this oxidation and no additional information was obtained from oxidation chronopotentiometry.

To conclude, chronopotentiometry indicates that the major effect of thorium is on the rate of reaction at the electrode and not on the transfer coefficient. The rate of reaction at an electrode

TABLE 7. THE EFFECT OF THORIUM PERCHLORATE ON THE
TRANSFER COEFFICIENT FOR THE REDUCTION OF IRON III AT A
PLATINUM ELECTRODE FROM THE DATA FOR FIGURE 33

<u>$[\text{Th}^{+4}]$</u> <u>moles/liter</u>	<u>Transfer Coefficient</u>
0.00164	0.34 \pm 0.02
0.00327	0.31 \pm 0.01
0.00654	0.31 \pm 0.01
0.0164	0.33 \pm 0.01
0.0327	0.34 \pm 0.01
0.0980	0.35 \pm 0.01

depends on the exchange current while the transfer coefficient is more characteristic of the mechanism. This means that, on the basis of chronopotentiometric measurements, thorium decreases the exchange current at the electrode without greatly changing the mechanism for the reduction of iron III.

EXPERIMENTAL

The cell shown in Figure 34 was used for chronopotentiometry. The working electrode consisted of a small piece of platinum wire sealed in soft glass tubing. The counter electrode was a cylindrical platinum gauze electrode which surrounded the working electrode. Because the reference electrode (S.C.E.) was outside the counter electrode the measured potentials include the IR potential drop between the working and counter electrodes. This potential drop was not more than a few millivolts. The constant current source consisted of an appropriate resistor placed in series with two Eveready W350 45 volt batteries. The potential of the working electrode was measured by using the Metrohm Polarecord as a high input resistance potential recorder. The current used for chronopotentiometry was measured in separate experiments by using the Polarecord as a galvanometer.

After deaeration the iron solutions were allowed to stand for seven minutes, to minimize convective effects, before a chronopotentiogram was obtained. Solutions were deaerated before each chronopotentiogram was obtained and usually three chronopotentiograms

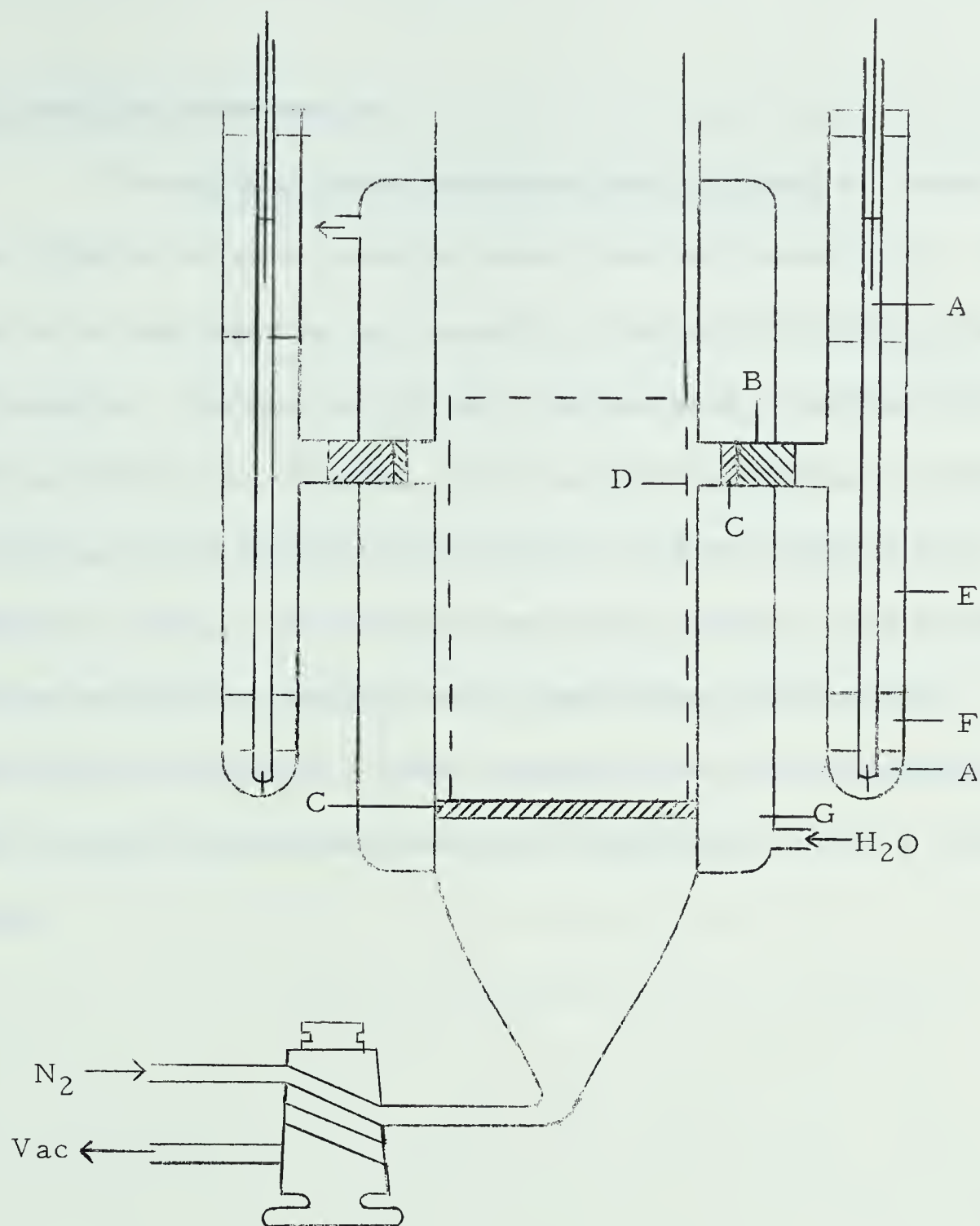


Figure 34. General purpose electrochemical cell. A, mercury; B, agar plug; C, porous glass frit; D, cylindrical platinum gauze electrode; E, saturated KCl; F, Hg₂Cl₂, KCl; G, thermostating water jacket.

were taken for each solution.

Ferric perchlorate solutions were prepared by heating ferric chloride to fuming with perchloric acid until nearly dry. This evaporation was repeated until a test for chloride with silver nitrate was negative. Ferrous perchlorate was prepared according to (27) starting with ferrous chloride. Ferrous perchlorate was recrystallized by utilizing its low solubility in perchloric acid as compared to its solubility in water. The ferrous perchlorate was also chloride free. Ferrous perchlorate solutions were standardized with standard potassium permanganate. Other reagents were as described previously except that deionized water was redistilled to remove traces of resin.

THE EFFECT OF THORIUM ON THE EXCHANGE CURRENT DENSITY
FOR THE FERRIC-FERROUS COUPLE

In determining parameters for an electrode reaction, an alternative to chronopotentiometry, where diffusion conditions are well defined, involves working under conditions such that the effects of diffusion are negligible. This means that the potential region studied is at the beginning of a current voltage curve where changes in concentration of reactant are negligible and the concentration of reactant at the electrode surface can be assumed to be constant with small changes in potential.

The procedure used for this study consisted of forcing small currents (in relation to the diffusion current) through the electrode and recording the deviation of the electrode potential, from its equilibrium value, caused by the current pulse. This current pulse method was used primarily for reasons of experimental simplicity.

The following equation can generally be applied to an electrode reaction (15)

$$i = i_o (e^{-\alpha n f \eta} - e^{(1 - \alpha) n f \eta})$$

i = Net current

i_o = Exchange current

α = Transfer coefficient

f = F/RT (16.9)

η = Overvoltage

This equation can be rearranged to give (18)

$$\ln \frac{i}{1 - e^{nf\eta}} = \ln i_o - \alpha nf\eta$$

so that if $\ln \frac{i}{1 - e^{nf\eta}}$ is plotted against the overvoltage a straight

line should result with slope equal to $-\alpha nf$ and intercept at $\ln i_o$.

There is no restriction as to size of the overvoltage to which this equation may be applied.

Figure 35 shows a typical plot of $\ln \frac{i}{1 - e^{nf\eta}}$ against

the overvoltage from Table 8. It is apparent that a linear relation exists between these two quantities. Generally speaking the most nearly straight lines were obtained when the electrode was aged and the overvoltages were large (at least 0.04 volts). With more active electrodes the points were more scattered but it was still possible to obtain reasonably good straight lines (Figure 36). If the electrode was very active it was not possible to obtain data that was satisfactory for straight line plots. To obtain satisfactory results with a very active electrode the equipment used must provide for more careful

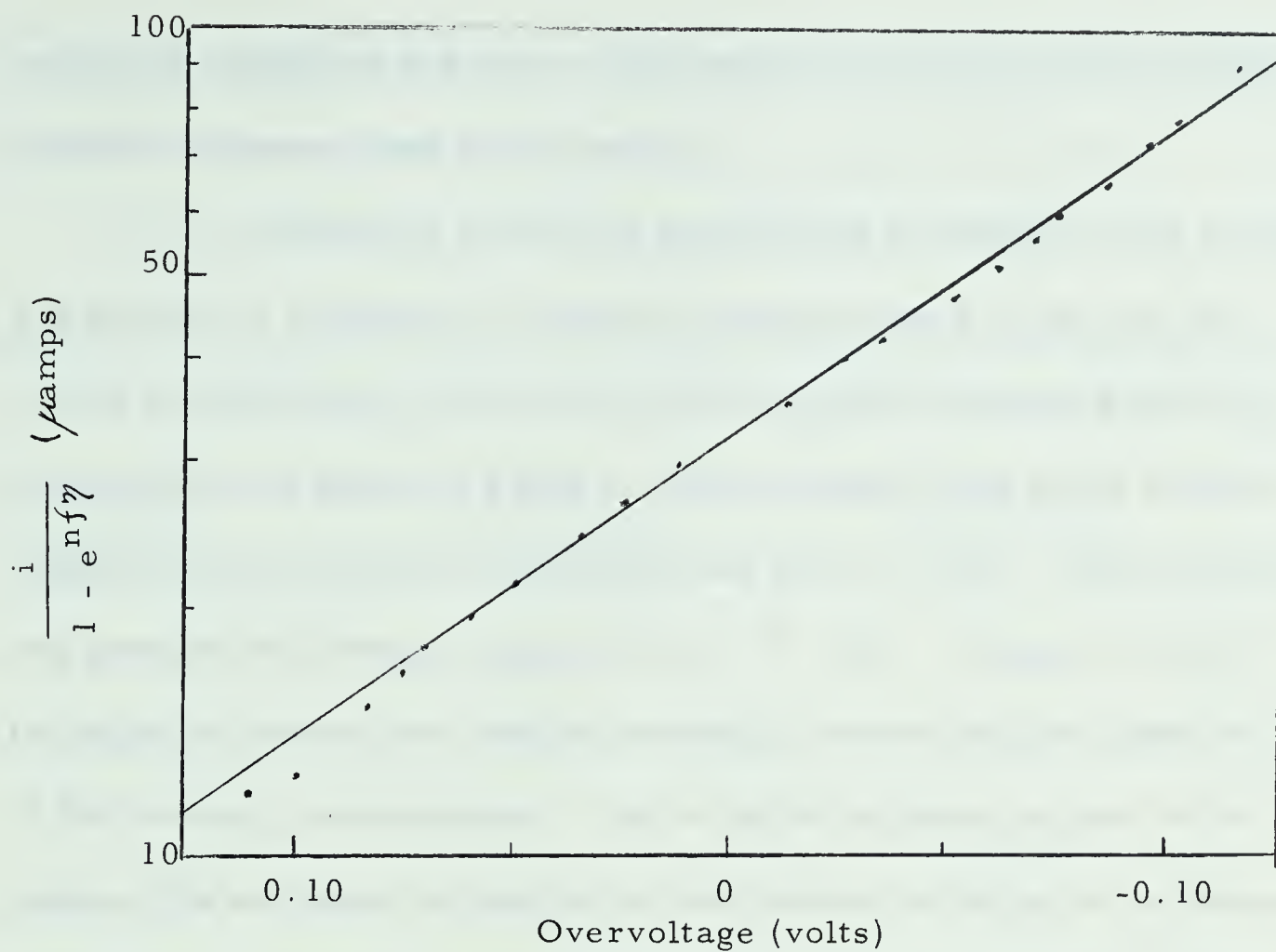


Figure 35. The relation between $\frac{i}{1 - e^{nf\eta}}$ and overvoltage for an aged platinum electrode.

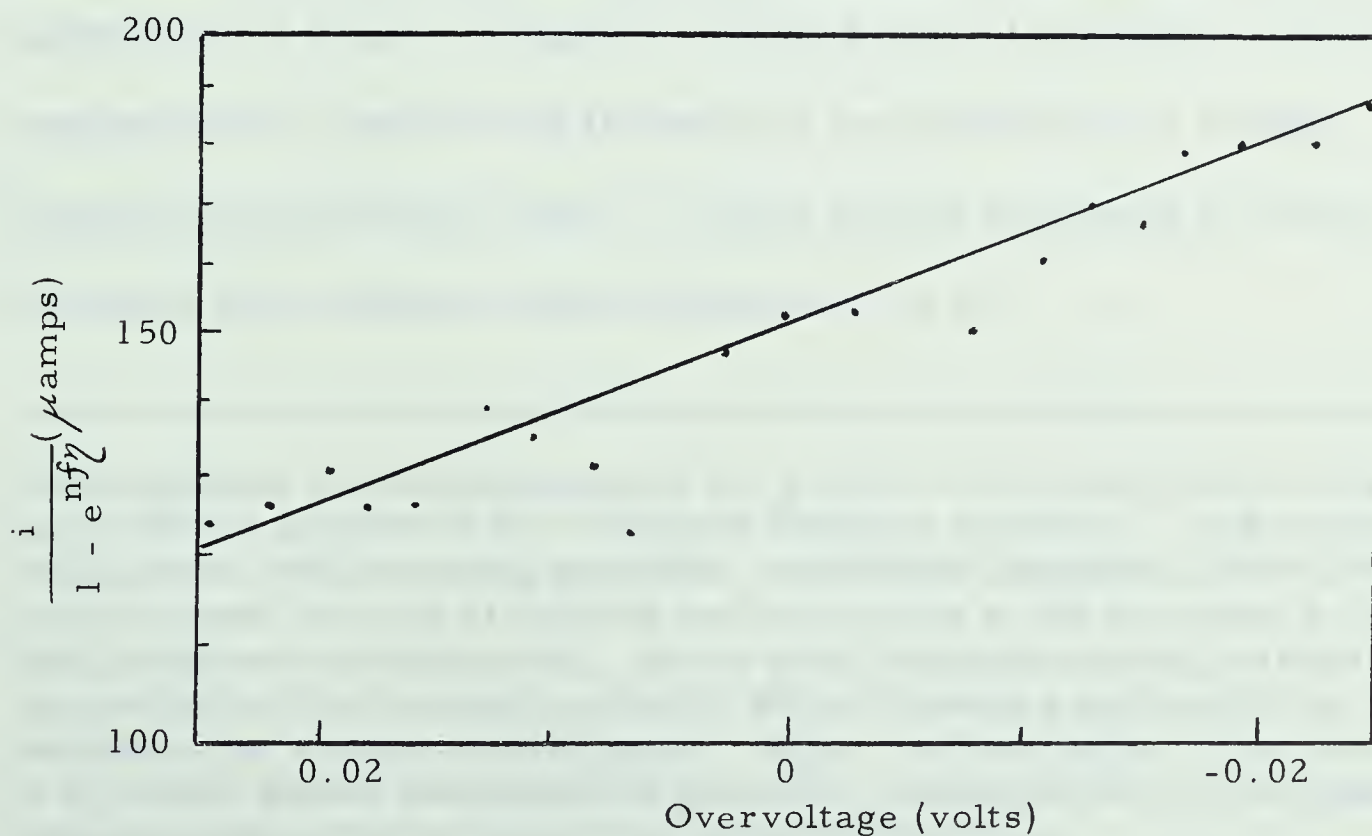


Figure 36. The relation between $\frac{i}{1 - e^{nf\eta}}$ and overvoltage for a more active platinum electrode.

control of conditions and more rapid measurements than was possible with the equipment used in this study.

The effect of thorium perchlorate at constant ionic strength was studied by alternately conducting measurements on an iron III - iron II solution then on an iron III-iron II solution containing thorium. The results are shown in Table 8. The average value of the transfer coefficient when thorium was absent was 0.26 ± 0.02 . When thorium was present the average value was 0.21 ± 0.01 . Figure 37 shows the relation between the relative exchange current and the logarithm of the thorium concentration. The relative exchange current is the ratio of the exchange current in an iron thorium solution to the average value of the exchange current in the thorium-free iron solutions that were measured preceeding and following the thorium solution. It is apparent from Figure 37 that the relation between the relative exchange current and the logarithm of the thorium concentration is a straight line within experimental error. This is not too surprising in view of the linear plots obtained earlier (Figures 23 to 26).

The maximum current pulses used for a given iron concentration were ten to fifteen percent of the estimated diffusion currents. Had concentration polarization been occurring the author would have expected a noisy potential measurement because of stirring and convection at the electrode surface. Such noise was not observed. It was also found that during passage of a current pulse the electrode potential did not change significantly for a few seconds after rotation was stopped. After the first three or four seconds of a current pulse, the change in potential, caused by the current pulse, did not usually drift by more than one or two percent.

TABLE 8. THE EFFECT OF THORIUM ON THE EXCHANGE CURRENT AND TRANSFER COEFFICIENT FOR THE FERRIC-FERROUS COUPLE AT A PLATINUM ELECTRODE

<u>Th(ClO₄)₄ moles/liter</u>	<u>Nominal Exchange Current $\mu\text{amp}/\text{cm}^2$</u>	<u>Transfer Coefficient</u>
-	520	0.24
3.00×10^{-3}	210	0.21
-	350	0.25
7.00×10^{-3}	250	0.22
-	450	0.27
1.00×10^{-2}	210	0.22
-	530	0.26
1.30×10^{-2}	200	0.21
-	610	0.27
1.50×10^{-2}	220	0.20
-	680	0.28
2.00×10^{-2}	210	0.20
-	730	0.28
3.00×10^{-2}	160	0.22
-	800	0.28

All solutions were 0.10M HClO₄; 0.01M Fe(ClO₄)₃; 0.01M Fe(ClO₄)₂. In addition Th(ClO₄)₄ was added as shown above. Constant ionic strength of 0.8 was maintained by the addition of NaClO₄.

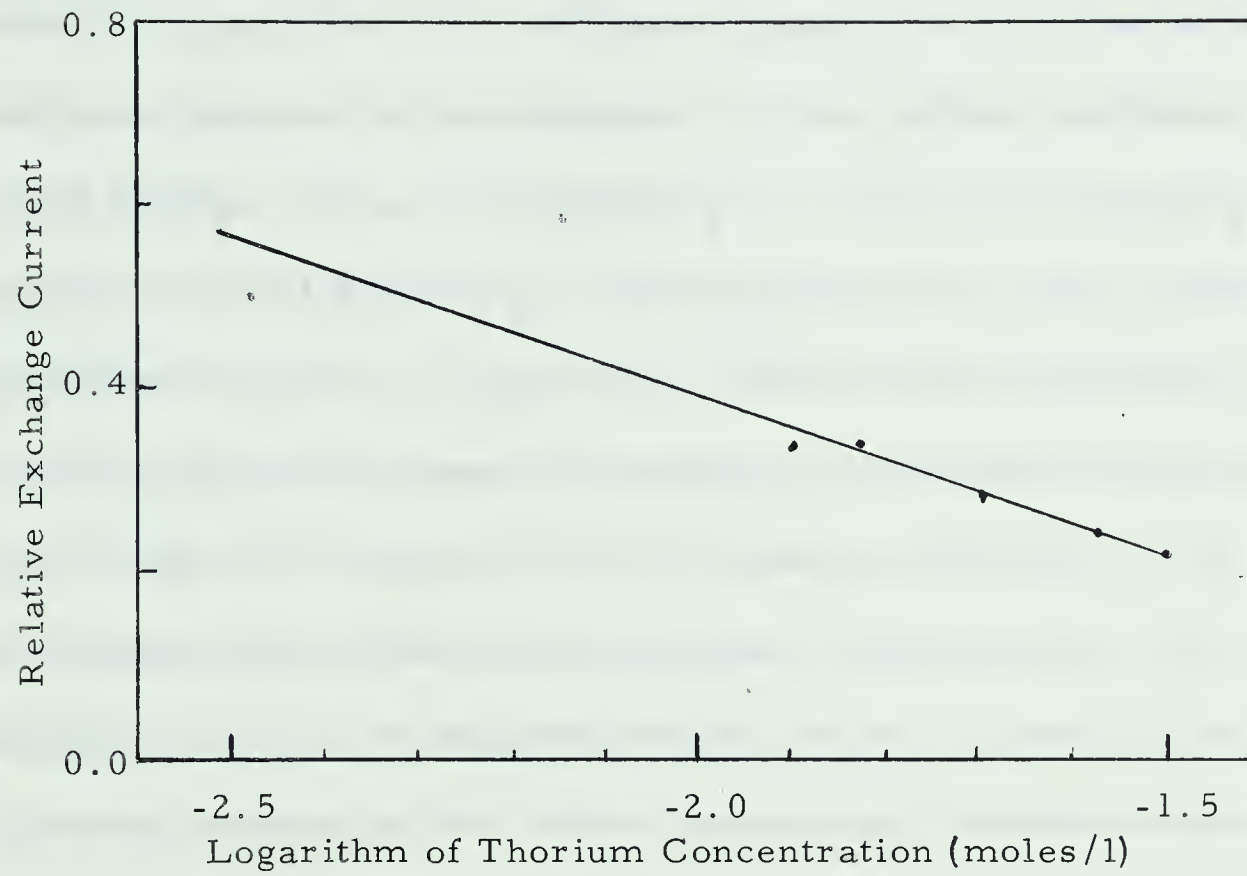


Figure 37. The relation between relative exchange current and (log of) thorium concentration (Table 8).

A COMPARISON OF CHRONOPOTENTIOMETRY AND THE CURRENT PULSE TECHNIQUE

The technique of using current pulses provided an opportunity to compare transfer coefficients obtained by chronopotentiometry with those obtained by this technique. For a solution containing 0.10M HClO_4 ; $1.00 \times 10^{-3}\text{M}$ $\text{Fe}(\text{ClO}_4)_3$; $1.00 \times 10^{-3}\text{M}$ $\text{Fe}(\text{ClO}_4)_2$ and $3.00 \times 10^{-3}\text{M}$ $\text{Th}(\text{ClO}_4)_4$. Chronopotentiometry gave transfer coefficients of 0.26, 0.26 and 0.25. For the same solution the current pulse method, used alternately with chronopotentiometry, gave values of 0.24 and 0.23 for the transfer coefficient. This agreement is well within the expected experimental error. The agreement between chronopotentiometry and the current pulse work is further evidence for the validity of measuring transition time as described previously.

SURFACE EFFECTS AND EXCHANGE CURRENT

Anodic polarization of a platinum electrode produces an oxide film on the electrode. This film is fairly stable in perchloric acid solutions of iron II-iron III (1), so an attempt was made to study the effect of thorium on the ferric-ferrous couple at an oxidized electrode. These experiments were not successful. When the electrode had an oxide film on it linear plots of $\ln \frac{i}{1 - e^{-n\eta}}$ against

overvoltage could not be obtained. This condition also persisted for several minutes after the electrical reduction of an oxide film. This oxidation-reduction cycle produces a lightly platinized electrode surface. Such a surface is extremely active and will consequently have a high exchange current density. A complete set of current pulse measurements required 10 to 15 minutes. There are a number of possible reasons why linear plots could not be obtained immediately after an oxidation-reduction cycle. 1. The activity of the electrode surface probably changed with time. 2. Trace amounts of oxide may have remained on the surface. 3. Surface contamination by slow impurity adsorption may have occurred. Probably a combination of these effects was involved. The surface of the electrode used for these studies was oxidized, reduced and then aged for about one-half hour. The surface could therefore be described as slightly aged or moderately active. This surface was not stable as is shown by the slow regular increase in the exchange current for an iron III-iron II solution of constant concentration as shown in Table 8. The exchange current values in Table 8 may be compared with those of Anson who obtained a value of about $10^4 \mu\text{amp}/\text{cm}^2$ for a similar iron concentration (2). This agreement is satisfactory in view of the uncertainty about the electrode area and the fact that the electrode used for the results in Table 8 was almost certainly less active than the electrode used by Anson,

TABLE 9. THE EFFECT OF A FIXED CONCENTRATION OF THORIUM
ON THE EXCHANGE CURRENT FOR THE FERRIC-FERROUS COUPLE

<u>$\text{Fe}(\text{ClO}_4)_3 - \text{Fe}(\text{ClO}_4)_2$</u> <u>moles/liter</u>	<u>$\text{Th}(\text{ClO}_4)_4$</u> <u>moles/liter</u>	<u>Exchange Current</u> <u>$\mu\text{amp/cm}$</u>
3.00×10^{-3}	0	5.3×10^2
3.00×10^{-3}	1.00×10^{-2}	2.1×10^2
1.00×10^{-2}	0	1.3×10^3
1.00×10^{-2}	1.00×10^{-2}	0.45×10^3
3.00×10^{-2}	0	2.0×10^3
3.00×10^{-2}	1.00×10^{-2}	1.1×10^3

Constant ionic strength of 0.75 was maintained with sodium perchlorate.

The effect of a given concentration of thorium perchlorate on the exchange current for various concentrations of iron III and iron II was studied. The relative change in exchange current caused by a fixed thorium concentration changes only slightly with the iron III-iron II concentration. Table 9 shows that a thorium concentration of 1.0×10^{-2} moles/liter reduced the exchange currents by 60%, 53% and 45% for iron III-iron II concentrations of 3.00×10^{-3} M, 1.00×10^{-2} M and 3.00×10^{-2} M. If this trend is real it is what one would expect since a large iron concentration should compete favourably with a small thorium concentration.

It is usually assumed that the exchange current is a linear function of concentration (2). It is obvious from Table 9 that this is not true for this particular system. This has been noted previously (2) and it has been suggested that this effect could be attributed to adsorbed iron.

In conclusion these current pulse studies indicate that the primary effect of thorium is on the exchange current while the transfer coefficient for the ferric-ferrous couple is only slightly affected by thorium.

EXPERIMENTAL

The platinum electrode used for these studies consisted of a platinum wire sealed in soft glass. The nominal surface area of the wire was 0.15 cm^2 . The device used to provide constant currents

at several different levels is shown in Figure 38 . The cell used is shown in Figure 34 .

The electrode was rotated during each set of measurements to help eliminate polarization. Anodic and cathodic currents were used alternately at each current level. The duration of each current pulse was about 15 seconds and the potential displacement was recorded using the Metrohm Polarecord. Usually eleven current pulses ranging from about 5 to 75 μ amps were used for each set of measurements. Two or three sets of measurements were carried out on each solution.

Because the measured electrode potential displacement included the IR drop it was necessary to correct this voltage for the IR drop. The IR correction was usually a few percent of the measured potential displacement. The resistance between the working and counter electrodes was measured with a conductance bridge. Sodium perchlorate was used to maintain constant ionic strength.

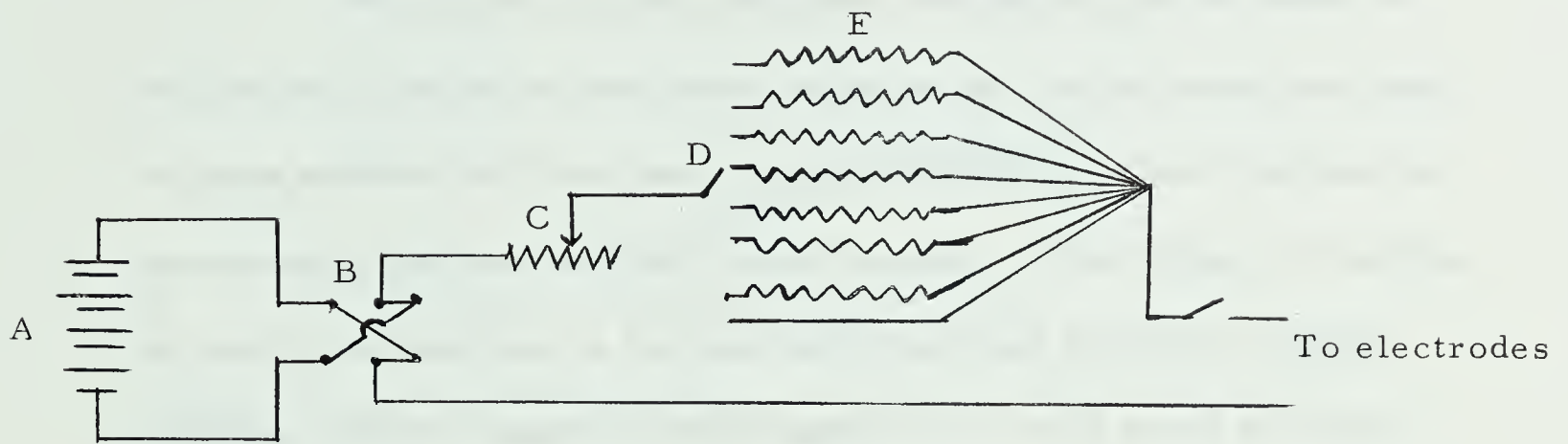


Figure 38. Apparatus used to provide constant currents.

A, Exide H0006 battery tapped to provide 48, 60, 72, 108 and 120 volts; B, dpdt switch; C, variable resistor 0 to 10 meg ohms; D, twelve position switch; E, eleven resistors ranging from 0.8 to 9 megohms.

DISCUSSION

SOME BACKGROUND INFORMATION

Not many studies have been carried out on the effect of non reactive cations on electrode reactions at a solid metal electrode. In those studies that have been reported the effect of such cations on the exchange current is small (a few percent). The effects of cations on electrode reactions at the mercury electrode have been studied but these effects cannot be easily applied to a solid metal electrode.

The effects of certain cations and anions on the exchange current for the quinone-hydroquinone system have been studied (39). Potassium, ammonium, rubidium and cesium ions all reduced the exchange current as did the halide anions and some alcohols. The effect of the anions and alcohols was attributed to adsorption while the cation effect was ascribed to changes in the double layer structure. Because cations can adsorb (3) it seems reasonable to the author that at least part of the cation effect on the quinone-hydroquinone exchange current might be due to adsorption.

The cation present in solution affects the evolution of oxygen at an electrode surface in aqueous solutions (21). If one plots voltage against the logarithm of the current the relation shown in Figure 39 is obtained.

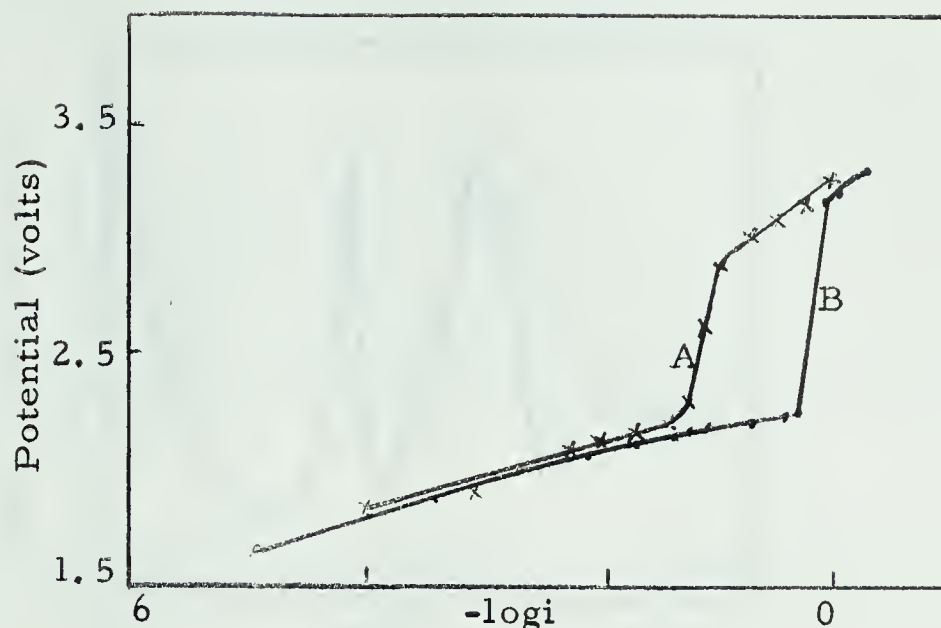


Figure 39. The relation between electrode potential and current for oxygen evolution at a platinum electrode.

Curve A of Figure 39 was obtained (3) using a solution $10^{-2}N$ $KClO_4$, $1.34N$ $HClO_4$. For curve B the solution contained only $1.34N$ $HClO_4$. The shift of the break in these curves has been discussed in some detail by Frumkin (3). A break in the potential-log current curve, for oxygen evolution, occurs when the electrode is covered with an oxygen monolayer. At the point of monolayer oxygen coverage metal cations are adsorbed through a dipole such as $M^+ \begin{smallmatrix} \delta^- & \delta^+ \\ O & -Pt \end{smallmatrix}$. This is equivalent to saying that the electrode potential is more negative than the potential of null charge for a platinum oxide electrode. The adsorbability of a particular cation determines when the surface is covered and this in turn influences the current density at which the break in the curve takes place.

Balashova and Merkulova carried out an extensive radio-chemical study of adsorption (3). Figure 40 is taken from their work:

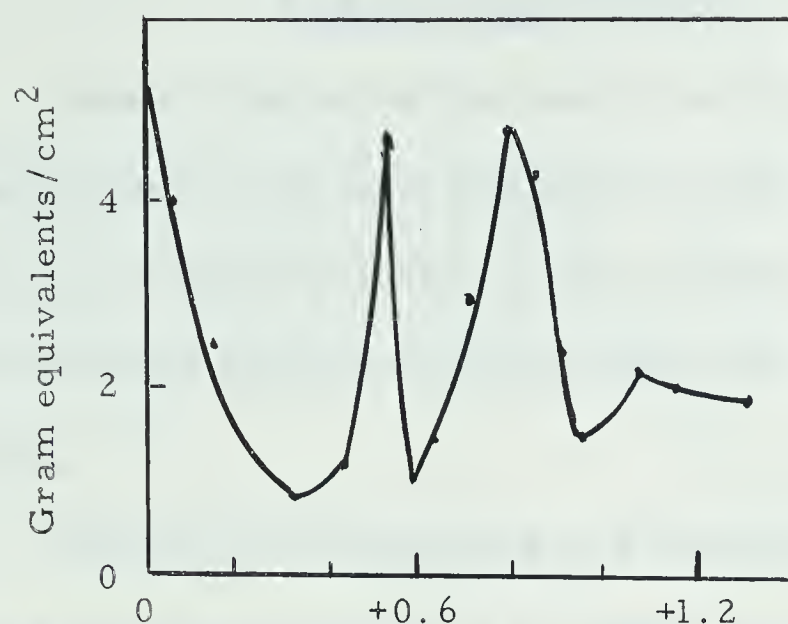


Figure 40. Electrode Potential (vs N.H.E.). The potential dependence of cesium adsorption.

and shows the potential dependence of cesium adsorption on platinum. To quote (3) "the relation of the adsorption of anions and cations on platinum to its potential is much more complex than was considered previously". These authors explained their results by postulating cation adsorption enhanced by a combination of anion adsorption and oxygen dipole adsorption. No detailed explanation for the various peaks given in Figure 40 was given.

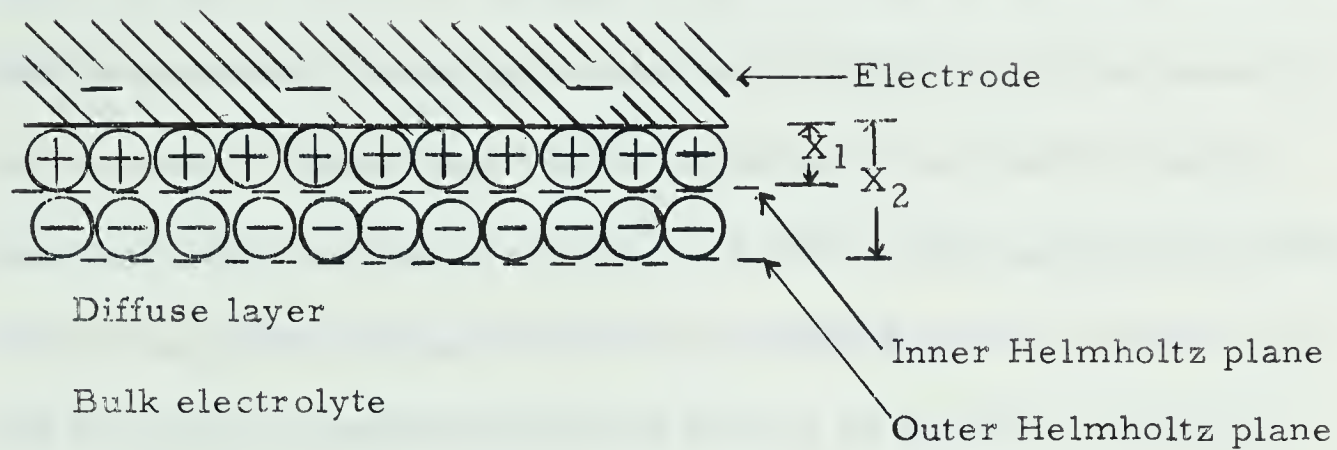
Obrucheveva (29) studied cation adsorption on platinum and gold electrodes at positive potentials by a technique called potential displacement. She found evidence for the adsorption of Tl^+ , Cd^{++} , Pb^{++} and Zn^{++} on platinum and gold electrodes at potentials between +0.3 and +0.7 volts (vs N.H.E.). This adsorption required several minutes to reach equilibrium. On the basis of this technique she concluded that, thorium did not adsorb on a platinum electrode.

ELECTRODE KINETICS

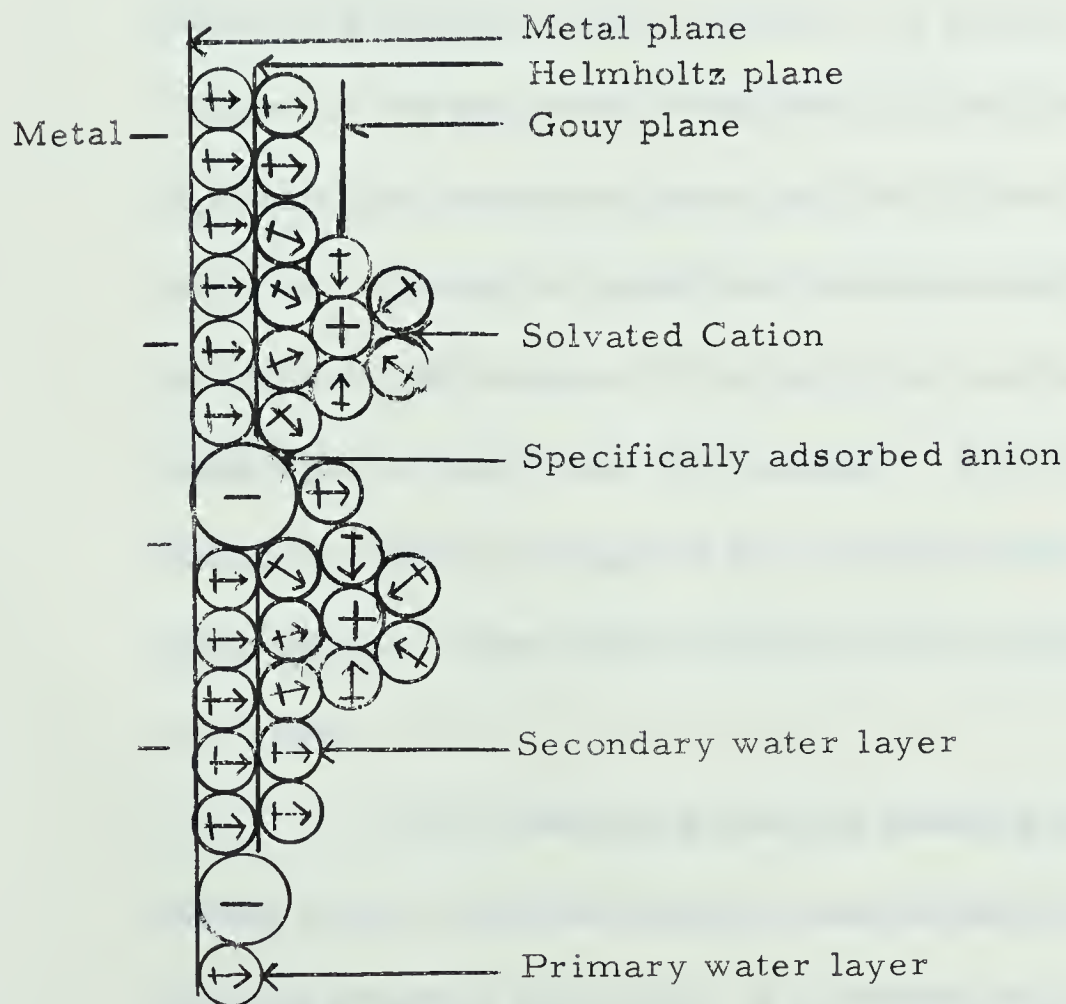
Many things affect the rate of an electrode reaction. The following discussion will be concerned only with those phenomena that occur at or very near the surface of an electrode. Chemical reactions that occur at some distance from the surface of the electrode are not considered.

As was originally noted by Frumkin (17a) any species that reacts at an electrode must be in the double layer at the electrode surface before it can react. This means that the double layer exerts an influence on nearly every electrode reaction. Early idealized models for the double layer envisaged a layer of adsorbed ions at the electrode surface; next a layer of counter ions; followed by a diffuse layer (Figure 41A). A more recent double layer model is that of Bockris, Devanathan, and Muller (5) who proposed a hydrated surface with oriented solvent dipoles as depicted in Figure 41B. They further proposed that specifically adsorbed anions could penetrate the inner plane while solvated cations remain outside this plane of oriented water. These idealized models are reasonably applicable to the mercury electrode. At solid metal electrodes the situation is more complex.

At solid metal electrodes the electrode kinetics are much more complicated because the surface of a solid electrode is neither smooth nor uniform. Even at the point of zero charge hydrogen and



A



B

Figure 41. Double layer models.

oxygen are both adsorbed on a platinum electrode immersed in an aqueous solution (17). At any other potential one of these substances will be adsorbed in addition to ions that are electrically attracted to the surface. These facts, combined with the fact that the heterogeneous platinum surface will have its own specific adsorption tendencies make it apparent that quantitative calculations about the double layer and its effect on electrode kinetics are not as feasible as they are with a mercury electrode.

The double layer has two primary effects on the rate of an electrode reaction (6). First, the double layer can alter the effective potential available for the reaction of a species from solution. Second, changes in the structure of the double layer can change the concentration of reactant in the double layer and this in turn changes the rate of reaction. Finally at solid heterogeneous electrodes the rate of reaction can be reduced if the electrode surface is blocked by some species other than the reactant. This blocking effect should be more properly thought of as a surface effect rather than a double layer effect. These three effects will be considered as they apply to this study.

If it is assumed that the reacting species does not approach closer to the electrode than the outer Helmholtz plane (Figure 41A) then the potential difference ϕ_2 between the electrode and the outer Helmholtz plane is not available to a reacting species from the bulk of

solution. This means that at negative potentials cation adsorption makes the available potential less than the applied potential and similarly for anion adsorption at positive potentials.

It is difficult to calculate the change in concentration of a species in a double layer that results from a change in double layer structure. This is especially true at solid electrodes where the structure of the double layer is uncertain. It is reasonable to assume however, that the various anions and cations in solution will compete for positions in the double layer and that if certain anions and cations are strongly attracted into the double layer then other anions and cations will be excluded from it.

Because the surface of a platinum electrode is heterogeneous it is reasonable to assume that the rate of an electrode reaction is much greater at some points on the electrode surface than at other points. Out of this surface heterogeneity the concept of active sites has arisen. These sites are envisioned as being responsible for a disproportionately large part of the electrode reaction. Blocking these sites will greatly reduce the rate of an electrode reaction even though only a small fraction of the surface is covered. These sites may be envisioned as having a high adsorption energy for the reacting species (21). This active site concept contradicts the idea that the rate of

reaction is directly proportional to surface area. The more correct concept depends on the electrode being used and the reaction under study.

The reduction of ferric ions and the oxidation of ferrous ions proceeds via a single electron transfer and the surface of the electrode is not altered by deposition of a solid. Despite the apparent simplicity of this redox reaction the exact mechanism is not known. The latest evidence (2) indicates that the reaction occurs by two paths: one involving loosely adsorbed iron and the other unadsorbed iron. Bockris, Devanathan, and Muller in discussing electron transfer reactions say "transfer of charge outside the first water layer seems difficult to accept for then the ion is sufficiently far away that the heat of activation associated with the transfer would be prohibitive" (15). On the basis of this statement it is reasonable to suggest that the electron transfer to or from the iron occurs when the water of hydration of the iron is, either incorporated into the primary water layer, or is next to the primary water layer (Figure 41B).

THE IRON-THORIUM SYSTEM

It has been experimentally established that the following are the primary effects of thorium on the oxidation-reduction reaction of the ferric-ferrous couple.

1. There is little effect of thorium on the diffusion current of a reversible current voltage curve for iron III.

2. If the current voltage curve for iron III is irreversible the effect of thorium is much greater.
 3. Thorium does not affect the standard potential of the ferric-ferrous couple measureably (± 5 mv).
 4. Increasing ionic strength decreases the effect of thorium on the reduction of iron III at a platinum electrode.
 5. Thorium slightly reduces the transfer coefficient but its main effect is on the exchange current for the ferric-ferrous couple.
- The implications of these experimental observation are discussed below.

To quote Delahay (16) "It is seen that the distinction between reversibility and irreversibility is quite arbitrary and depends on the relative magnitude of the exchange and limiting currents." As long as the exchange current remains larger than the diffusion current the current voltage curve will appear reversible. Thus if thorium lowers the exchange current to a value below the diffusion current the current voltage curve will become irreversible. If the initial exchange current is large and it is not lowered to a value near the diffusion current the reversible current voltage wave will not appear to be affected even though the exchange current has been reduced. This explains why vigorous cleaning of the electrode removes the thorium effect from a current voltage curve. Cleaning activates the surface of the electrode without particularly affecting the diffusion

current. Under these circumstances the lower value of the exchange current, after the addition of thorium is still larger than the diffusion current and therefore the current voltage wave remains apparently reversible when thorium is present.

The addition of thorium to a solution of iron III reduces the iron III reduction current. This effect could be explained by assuming that the potential difference between the bulk of the solution and the point in the double layer where iron III is reduced is altered by thorium in such a way as to reduce the rate of reduction of iron III. Such a shift in available potential would increase the rate of oxidation of iron II. Since thorium decreases the rate of oxidation of iron II it would seem that the major effect of thorium is not an alteration of available potential. This assumes that the effect of thorium on the double layer is not especially sensitive to the potential of the platinum electrode. This is a reasonable assumption (15).

The effect of increasing ionic strength can be explained by postulating that a large concentration of sodium ions effectively competes with a low concentration of thorium ions, and that sodium ions do not interfere with the reduction of iron III to the same extent that thorium

does.

Two effects still to be considered as explanations for the thorium effect are changes in the concentration of iron in the double layer and a blocking of active sites on the electrode surface. If the major effect is blocking of active sites then the thorium must be only loosely adsorbed for reasons mentioned earlier. It is probably not possible to distinguish between a loosely adsorbed thorium ion and a thorium ion in the double layer.

The property that sets the thorium ion apart from most cations is its high charge. This means that thorium has strong attractive and repulsive electrical forces, and assuming that hydration depends largely on charge (8) the hydrated thorium cation will be larger than most other cations. The author proposes that the high charge carried by thorium means that it will be drawn into the double layer more strongly than other cations. Once it is in the double layer both the size and charge of the thorium ion will tend to exclude other cations from the double layer. Since the exchange current is proportional to the concentration of iron in the double layer (26) the exchange current is then reduced because the concentration of iron in the double layer is then reduced.

If the explanation in the preceding paragraph is correct other cations with a charge of 4 should produce a similar effect. Cations with a lesser charge should have a smaller or negligible

effect. Cations as highly charged as thorium are not common and some that do exist either hydrolyze readily or are electrochemically active themselves so that it would be difficult to study their effect on another electrode couple. This effect of thorium should also exist with couples other than the ferric-ferrous one. This study was restricted to the ferric-ferrous couple because it involves a one electron transfer and no reaction product is deposited on the electrode surface. However another investigator has indicated that thorium also makes the reaction $\text{Cu}^{++} + 2e \longrightarrow \text{Cu}$ more irreversible at a platinum electrode (11).

CONCLUSION

In conclusion the effect of thorium on the reduction of iron III and the oxidation of iron II has been studied using current voltage curves, radiochemical adsorption, chronopotentiometric, and current pulse techniques. On the basis of the accumulated experimental information it has been concluded that the primary effect of thorium on the ferric-ferrous couple is exclusion of iron from the double layer and a blocking of active sites on the electrode surface with a resultant decrease in the exchange current for the iron couple. It is probable that thorium produces this effect because of its high charge.

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APPENDIX

Dr. F. Anson (Professor, California Institute of Technology and External Examiner) raised the following questions. Does thorium exist in the $+4$ state? Could the effect of the thorium be attributed to the flocculation of an iron III colloid by thorium?

In reply the author wishes to state that several investigators have studied the hydrolysis of thorium (1, 2, 3). Kraus and Holmberg (2) state that Th^{+4} does exist in aqueous solutions these authors give the following equilibrium constants.

$$\frac{[\text{Th}(\text{OH})^{+3}] [\text{H}_3\text{O}^+]}{[\text{Th}^{+4}] [\text{H}_2\text{O}]^2} = 5 \times 10^{-5}$$

$$\frac{[\text{Th}(\text{OH})^{+2}] [\text{H}_3\text{O}^+]}{[\text{Th}^{+4}]} = 3 \times 10^{-8}$$

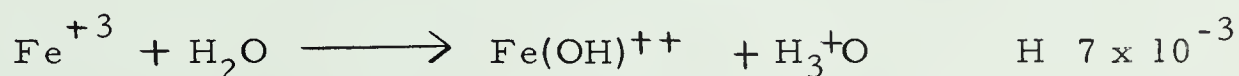
Other investigators report values of 1×10^{-4} and 1×10^{-9} for these same equilibria (3).

These constants indicate that in 0.1M acid only about 0.5% of the thorium would be present as $\text{Th}(\text{OH})^{+3}$ and an even smaller amount of $\text{Th}(\text{OH})_2^{++}$ would be present. Even at pH values of two or three most of the thorium would still be present as Th^{+4} .

The experiment described on page 45 indicates that the higher iron III hydrolysis products do not yield an appreciable reduction current. The author suspects that had the iron III been present as a colloid almost no reduction current would have been obtained. It is

true that as the pH increases the effect of thorium becomes greater. The experiments with sodium perchlorate show that as the ionic strength of the solution decreases the effect of the thorium also becomes greater. As the pH increases the ionic strength becomes less so that at least part of the enhancement of the thorium effect with increasing pH must be attributed to decreasing ionic strength rather than the change in pH. Unfortunately no experimental work was done with constant ionic strength at various pH's. Had such work revealed that pH had a marked effect at constant ionic strength it would still not have been possible to state that the effect was solely due to pH since the effect of hydrogen ions on double layer structure would probably not be the same as the effect of other cations.

Milburn (5) gives the following equilibrium constant



so that in 0.1M acid about seven percent of the iron III is present as $\text{Fe}(\text{OH})^{++}$. Stock ferric perchlorate solutions were strongly acid. On making up solutions iron III was added to solutions that were already acid so that higher ion hydrolysis products had no opportunity to form.

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